

Supporting Information

Nickel-Catalyzed Direct Synthesis of Aryl Olefins from Ketones and Organoboron Reagents under Neutral Conditions

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Experimental procedures and compound characterization

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I. General Information

All NMR spectra were acquired on Bruker 500 MHz, 400 MHz or 300 MHz NMR spectrometers. ^1H NMR chemical shifts were recorded relative to TMS (δ 0.00) or residual protiated solvents (CDCl_3 ; δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a J value in Hz. ^{13}C NMR spectra were obtained at 125 MHz on 500 MHz, 100 MHz on 400 MHz or 75 MHz on 300 MHz NMR instruments and chemical shifts were recorded relative to solvent resonance (CDCl_3 ; δ 77.16). ^{19}F NMR spectra were recorded at 376 MHz on 400 MHz NMR spectrometers, 282 MHz on 300 MHz NMR without any external standard. The extent of deuterium was determined by quantitative ^1H NMR spectroscopy. Proof of purity of new compounds was demonstrated with copies of ^1H , ^{13}C , and ^{19}F NMR spectra.

Glassware was dried at 120 °C for at least 3 hours before use. Anhydrous diglyme (Aldrich) was degassed by argon bubbling and then stored over activated 4 Å molecular sieve beads in the glove box before use. Other solvents used in the solvent optimization were dried and purified according to the procedure from "Purification of Laboratory chemicals book". All of anhydrous solvents were stored in Schlenk tubes in the glove box. Unless noted otherwise, commercially available chemicals were used without further purification.

Flash chromatography was performed using Merck 40-63 D 60 Å silica gel. The desired product was purified directly by flash chromatography over silica gel using hexanes as the elute or a mixture of hexanes and ethyl acetate when the compound were more polar. The GC internal standard, *n*-dodecane was degassed and dried over activated 4 Å molecular sieve beads before use. GC analysis was performed on a Shimadzu GC-2010 instrument with Agilent J&W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI.

II. Condition optimization

A typical procedure: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with Ni(PPh₃)₄ (5 mol%, 5.5 mg, 0.005 mmol), 1,2-bis(dicyclohexylphosphino)ethane (6 mol%, 2.5 mg, 0.006 mmol) and 1 mL of dry diglyme. After stirring at room temperature for 5 minutes, acetophenone (12 mg, 0.1 mmol), phenylboroxine (16 mg, 0.05 mmol), H₂O (0.2 μ L) and GC standard *n*-dodecane (10 μ L) were then added sequentially via microsyringes. The tube was capped tightly and the reaction mixture was heated in an oil bath maintained at 110 °C for 1 day. At the end of the reaction, the mixture was cooled to room temperature. Aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of acetophenone and the calibrated yield of product. When HX salts of *N*-heterocyclic carbenes were used, they were stirred with an equimolar of NaO^tBu at RT for 30 min to release free carbenes and then stirred with Ni(PPh₃)₄ for 5 min before addition of other components (Table S1). In some entries, some byproducts derived from self-aldol condensation of the ketone was detected which accounted for material balance.

Table S1. Effect of supporting ligands

$ \begin{array}{c} \text{Ph}-\text{C}(=\text{O})-\text{CH}_3 + (\text{PhBO})_3 \\ \xrightarrow[\text{H}_2\text{O } 10 \text{ mol\%, diglyme}]{\text{Ni(PPh}_3)_4 \text{ 5 mol\% ligand 6 mol\%}} \\ 110 \text{ }^\circ\text{C, 24 h} \end{array} \rightarrow \begin{array}{c} \text{HO}-\text{C}(\text{Ph})_2-\text{Ph} \\ \text{Int} \end{array} + \begin{array}{c} \text{Ph}-\text{C}(\text{Ph})=\text{CH}_2 \\ \text{P} \end{array} $				
Entry	Added ligand	Conv of ketone (%)	Carbinol (%)	P (%)
1	None	5	0	0
2	PPh ₃	7	0	0
3	P(2-furyl) ₃	7	0	0
4	PCy ₃	9	0	0
5	P ^t Bu ₃	1	0	0
6	Davephos	9	0	0
7	XPhos	5	0	0

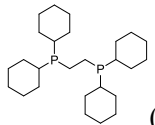
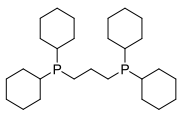
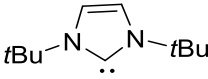
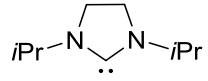
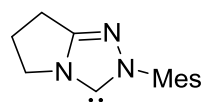
8	 (DCYPE)	100	1	99
9	 (DCYPP)	84	1	67
10	DPPE	6	0	0
11	DPPP	2	0	0
12	DPPB	9	0	0
13	DPPF	5	0	0
14	BINAP	9	0	0
15	DPEPhos	5	0	0
16	IPr	2	0	0
17	IMes	3	0	0
18		0	0	0
19		1	0	0
20		1	0	0

Table S2. Effect of Ni or Pd source

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{CH}_3 \end{array} + (\text{PhBO})_3 \xrightarrow[\text{H}_2\text{O 10 mol\%, diglyme}]{\text{metal 5 mol\%}, \text{DCYPE 6 mol\%}} \begin{array}{c} \text{HO} \\ \\ \text{Ph}-\text{C}-\text{Ph} \end{array} + \begin{array}{c} \text{Ph}-\text{C}=\text{CH}_2 \end{array} $ <p style="text-align: center;"> Int P </p> <p style="text-align: center;">110 °C, 24 h</p>				
Entry	Metal source	Conv of ketone (%)	Carbinol (%)	P (%)
1	Ni(PPh ₃) ₄	100	1	99
2	Ni(cod) ₂	41	2	33
3	Ni(acac) ₂	5	1	1
4	NiCl ₂ (PPh ₃) ₂	11	0	0
5	NiCl ₂ ·DME	4	0	0
6	Ni(OTf) ₂	44	4	6
7	Pd(PPh ₃) ₄	4	0	0
8	Pd(OAc) ₂	67	0	0
9	PdCl ₂	9	0	0
10	Pd ₂ (dba) ₃	55	0	0

Table S3. Effect of solvents

$ \text{Ph-C(=O)-CH}_3 + (\text{PhBO})_3 \xrightarrow[\text{H}_2\text{O 10 mol\%, solvent}]{\text{Ni(PPh}_3)_4 \text{ 5 mol\%}, \text{DCYPE 6 mol\%}} \text{Ph-C(OH)(Ph)-CH}_3 + \text{Ph-C(=CH}_2\text{)-CH}_3 $ <p style="text-align: center;"> Int P </p>				
Entry	Solvent	Conv of ketone (%)	Carbinol (%)	P (%)
1	Toluene	100	5	87
2	PhCF ₃	77	0	60
3	Anisole	100	0	85
4	Diglyme	100	1	99
5	Triglyme	86	4	71
6	Cyclopentyl methyl ether	100	2	84
7	THF	87	40	22
8	1,4-Dioxane	75	20	43
9	Acetonitrile	47	0	0

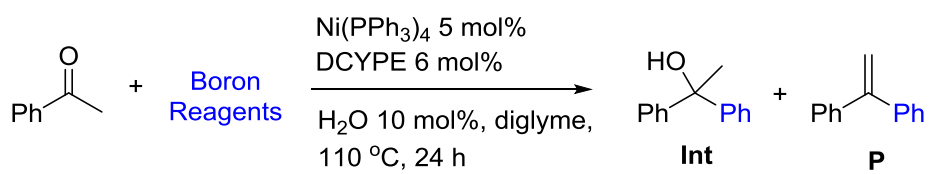
Table S4. Effect of water additive

$ \text{Ph-C(=O)-CH}_3 + (\text{PhBO})_3 \xrightarrow[\text{H}_2\text{O (X equiv.), diglyme, 110 }^\circ\text{C, 24 h}]{\text{Ni(PPh}_3)_4 \text{ 5 mol\%}, \text{DCYPE 6 mol\%}} $				
$ \text{Ph-C(OH)(Ph)-CH}_3 + \text{Ph-C(=CH}_2\text{)-CH}_3 $				
<div style="display: flex; justify-content: space-around; align-items: center;"> <div>Int</div> <div>P</div> </div>				
Entry	H ₂ O (equiv)	Conv of ketone (%)	Carbinol (%)	P (%)
1	none	100	1	89
2	0.1	100	1	99
3	0.5	39	0	32
4	1	15	1	8
5	3	6	3	0

Table S5. Use of CH₃CO₂H as additive

$ \text{Ph-C(=O)-CH}_3 + (\text{PhBO})_3 \xrightarrow[\text{AcOH X mol\%, diglyme, 110 }^\circ\text{C}]{\text{Ni(PPh}_3)_4 \text{ 5 mol\%}, \text{DCYPE 6 mol\%}} $					
$ \text{Ph-C(=CH}_2\text{)-CH}_3 + \text{Ph-C(=CH-CH}_3\text{)-C(=O)-CH}_3 $					
<div style="display: flex; justify-content: space-around; align-items: center;"> <div>P</div> <div>Aldol-BP</div> </div>					
Entry	AcOH (mol%)	Conv. of ketone (%)	Carbinol (%)	P (%)	Aldol (%)
1	10	34	0	0	16
2	20	33	0	0	12
3	50	27	0	0	13

Table S6. Effect of phenylboron reagents



$\text{Ph-C(=O)-CH}_3 + \text{Boron Reagents} \xrightarrow[\text{H}_2\text{O 10 mol\%, diglyme, 110 }^\circ\text{C, 24 h}]{\text{Ni(PPh}_3)_4 \text{ 5 mol\%, DCYPE 6 mol\%}}$

$\text{Ph-C(OH)(Ph)-CH}_3 + \text{Ph-C(=CH}_2\text{)-Ph}$

Int **P**

Entry	Boron reagent	Conv of ketone (%)	Carbinol (%)	P (%)
1	PhB(pin)	5	0	0
2	PhB(neop)	11	0	0
3	PhBF ₃ K	11	6	0
4	(PhBO) ₃	100	1	99
5	PhB(OH) ₂	19	3	2
6	PhB(cat)	48	0	19

A typical procedure: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with Ni(cod)₂ (5 mol%, 1.4 mg, 0.005 mmol), PPh₃ (20 mol%, 5.2 mg, 0.02 mmol) and 1 mL of dry diglyme. After stirring at room temperature for 5 minutes, 1,2-bis(dicyclohexylphosphino)ethane (6 mol%, 2.5 mg, 0.006 mmol) was added, and stirred at room temperature for another 5 minutes. Next, acetophenone (12 mg, 0.1 mmol), phenylboroxine (16 mg, 0.05 mmol), H₂O (0.2 μ L) and GC standard *n*-dodecane (10 μ L) were added sequentially. The tube was capped tightly and the reaction mixture was heated on an oil bath maintained at 110 °C for 1 day. At the end of the reaction, the mixture was cooled to room temperature. Aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of acetophenone and the calibrated yield of product.

In entry 5, Ni(cod)₂ and PPh₃ were stirred in 0.5 mL of hexane at rt for 10 min, then the solvent was removed under vacuum. The rest of the components and the solvent were added to initiate the catalytic reaction.

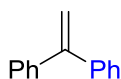
Table S7. Use of Ni(cod)₂ and PPh₃ in place of Ni(PPh₃)₄ in catalytic arylation

$ \text{Ph-C(=O)-CH}_3 + (\text{PhBO})_3 \xrightarrow[\text{H}_2\text{O 10 mol\%, diglyme, 110 }^\circ\text{C}]{\text{Ni(cod)}_2 \text{ 5 mol\%, PPh}_3 \text{ 20 mol\%, DCYPE 6 mol\%}} \text{Ph-C(=CH-Ph)-CH}_3 $					
Entry	PPh ₃ (mol%)	Solvent	Conv of ketone (%)	Carbinol (%)	P (%)
1	0	Toluene	41	0	33
2	0	Diglyme	43	0	29
3	20	Toluene	46	0	34
4	20	Diglyme	40	0	35
5	20	Diglyme	100	0	99

III. Isolation of products

(1) Reaction of ketones with phenylboroxine

A typical procedure: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with Ni(PPh₃)₄ (5 mol%, 11 mg, 0.01 mmol), 1,2-bis(dicyclohexylphosphino)ethane (6 mol%, 5 mg, 0.012 mmol) and 2 mL of dry diglyme. After stirring at room temperature for 5 minutes, acetophenone (24 mg, 0.2 mmol), phenylboroxine (31 mg, 0.1 mmol), H₂O (0.4 μ L added via a 5 μ L microsyringe) and GC standard *n*-dodecane (20 μ L) were then added sequentially. The tube was capped tightly and the reaction mixture was heated on an oil bath maintained at 110 °C for 1 day. The desired product was purified directly by flash chromatography over silica gel using hexanes as the elute or a mixture of hexanes and ethyl acetate when the compound were more polar. Similar results were obtained when the reactions were set up with a standard vacuum manifold and Schlenk tube.



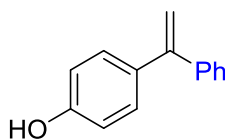
1,1-Diphenylethylene (3a) [530-48-3].¹

Colorless oil. 34 mg, 95% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.32 (m, 10H), 5.47 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 150.3, 141.7, 128.4, 128.3, 127.9, 114.4.

MS (EI): Calcd for C₁₄H₁₂: 180.1; found: 180.1.



p-Hydroxyl-1,1-diphenylethylene (3b) [17256-00-7].²

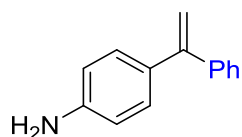
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 15:1 as eluent.

Colorless oil. 26 mg, 66% yield. When 1 equiv of phenylboroxine was used, the yield was increased to 89% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.35 – 7.32 (m, 5H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.40 (s, 1H), 5.36 (s, 1H), 4.82 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 155.4, 149.6, 141.9, 134.4, 129.8, 128.5, 128.3, 127.8, 115.1, 113.2.

MS (EI): Calcd for C₁₄H₁₂O: 196.1; found: 196.1.



***p*-Amino-1,1-diphenylethylene (3c) [46407-51-6].³**

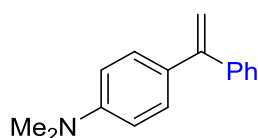
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 10:1 as eluent.

Colorless oil. 25 mg, 65% yield. When 1 equiv of phenylboroxine was used, the yield was increased to 82% after 24 h at 120 °C.

¹H NMR (300 MHz, CDCl₃): δ 7.38 – 7.30 (m, 5H), 7.19 – 7.14 (m, 2H), 6.67 – 6.63 (m, 2H), 5.38 (d, *J* = 1.4 Hz, 1H), 5.28 (d, *J* = 1.4 Hz, 1H), 3.71 (br s, 2H).

¹³C NMR (75 MHz, CDCl₃): δ 150.0, 146.3, 142.3, 131.9, 129.4, 128.6, 128.2, 127.7, 114.8, 112.0.

MS (EI): Calcd for C₁₄H₁₃N: 195.1; found: 195.1.



***p*-N,N-Dimethyl-1,1-diphenylethylene (3d) [22057-80-3].¹**

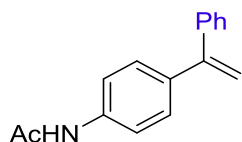
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent.

Colorless oil. 30 mg, 67% yield. When 1 equiv of phenylboroxine was used, the yield was increased to 84% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.29 (m, 5H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 5.37 (s, 1H), 5.25 (s, 1H), 2.97 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 150.4, 150.0, 142.5, 129.6, 129.2, 128.6, 128.2, 127.6, 112.1, 111.5, 40.7.

MS (EI): Calcd for C₁₆H₁₇N: 223.1; found: 223.1.



***p*-N-Acetamido-1,1-diphenylethylene (3e) [22101-32-2].¹**

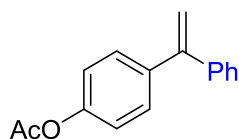
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 3:1 as eluent.

White solid. 20 mg, 42% yield due to incomplete conversion of the ketone (68% conversion).

¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.26 (m, 7H), 5.43 (s, 1H), 5.40 (s, 1H), 2.18 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 168.4, 149.5, 141.6, 137.64, 137.56, 129.0, 128.4, 128.3, 127.9, 119.7, 114.0, 24.8.

MS (EI): Calcd for C₁₆H₁₅NO: 237.1; found: 237.0.



***p*-Acetoxyl-1,1-diphenylethylene (3f).**

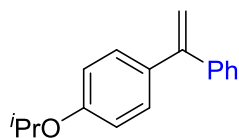
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent.

Colorless oil. 32 mg, 67% yield. When 1.0 equiv of phenylboroxine was used, the yield was increased to 91% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.32 (m, 7H), 7.08 – 7.05 (m, 2H), 5.46 (s, 2H), 2.32 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 169.6, 150.5, 149.4, 141.4, 139.3, 129.4, 128.41, 128.35, 128.0, 121.4, 114.6, 21.3.

MS (EI): Calcd for C₁₆H₁₄O₂: 238.1; found: 238.0.



***p*-Isopropoxy-1,1-diphenylethylene (3g).**

The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent.

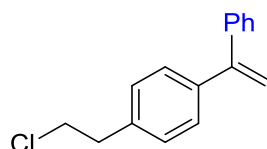
Colorless oil. 29 mg, 61% yield due to incomplete conversion of ketone (71%) under standard conditions.

When 1 equiv of phenylboroxine was used, the yield was increased to 89% after 24 h at 120 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.36 – 7.30 (m, 5H), 7.27 – 7.23 (m, 2H), 6.85 – 6.82 (m, 2H), 5.39 (d, J = 1.2 Hz, 1H), 5.33 (d, J = 1.2 Hz, 1H), 5.56 (hept, J = 6.0 Hz, 1H), 1.35 (d, J = 6.1 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 157.9, 149.8, 142.1, 133.9, 129.5, 128.5, 128.2, 127.8, 115.5, 112.9, 70.0, 22.3.

MS (EI): Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: 238.1; found: 238.1.



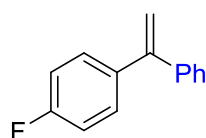
***p*-Chloroethyl-1,1-diphenylethylene (3h).**

Pale yellow oil. 24 mg, 50% yield due to incomplete conversion of ketone (55% conversion).

^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.30 (m, 7H), 7.19 (d, J = 8.1 Hz, 2H), 5.46 (d, J = 0.9 Hz, 1H), 5.44 (d, J = 1.0 Hz, 1H), 3.74 (t, J = 7.4 Hz, 2H), 3.09 (t, J = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 149.8, 141.6, 140.2, 137.8, 128.8, 128.6, 128.4, 128.3, 127.9, 114.3, 45.0, 39.0.

MS (EI): Calcd for $\text{C}_{16}\text{H}_{15}\text{Cl}$: 242.1; found: 242.1.



***p*-Fluoro-1,1-diphenylethylene (3i) [395-21-1].¹**

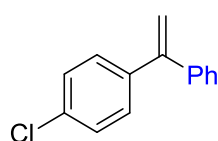
Colorless oil. 37 mg, 92% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.27 (m, 7H), 7.03 – 6.98 (m, 2H), 5.43 (s, 1H), 5.40 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 162.7 (d, J = 246.7 Hz), 149.2, 141.5, 137.7 (d, J = 3.3 Hz), 130.0 (d, J = 8.1 Hz), 128.4 (d, J = 5.3 Hz), 128.0, 115.3, 115.1, 114.3.

^{19}F { ^1H } NMR (376 MHz, CDCl_3): δ -114.7.

MS (EI): Calcd for $\text{C}_{14}\text{H}_{11}\text{F}$: 198.1; found: 198.1.



***p*-Chloro-1,1-diphenylethylene (3j) [18218-20-7].⁴**

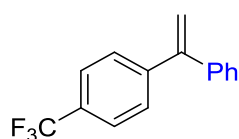
Colorless oil. 13 mg, 29% yield due to incomplete conversion of ketone (35% conversion).

When 1.0 equiv of phenylboroxine was used, the yield was increased to 42% with partial conversion of ketone (46%) after 24 h at 120 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.36 – 7.27 (m, 9H), 5.46 (s, 1H), 5.45 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3): δ 149.2, 141.2, 140.1, 133.8, 129.7, 128.5, 128.43, 128.35, 128.1, 114.8.

MS (EI): Calcd for $\text{C}_{14}\text{H}_{11}\text{Cl}$: 214.1; found: 214.1.



***p*-Trifluoromethyl-1,1-diphenylethylene (3k) [345-88-0].¹**

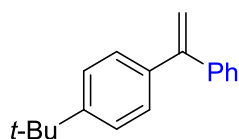
Colorless oil. 26 mg, 52% yield due to incomplete conversion of the carbinol. No byproducts were detected. When 1 equiv of phenylboroxine was used, the yield was increased to 86% after 24 h at 120 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.38 – 7.30 (m, 5H), 5.57 (d, J = 0.9 Hz, 1H), 5.52 (d, J = 0.8 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 149.2, 145.3, 140.8, 129.9 (q, J = 32.6 Hz), 128.7, 128.5, 128.3, 128.2, 125.3 (q, J = 3.8 Hz), 124.4 (q, J = 272.0 Hz), 116.0.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ -62.5.

MS (EI): Calcd for $\text{C}_{15}\text{H}_{11}\text{F}_3$: 248.1; found: 248.0.



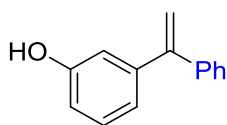
***p*-tert-Butyl-1,1-diphenylethylene (3l) [17582-85-3].⁴**

Colorless oil. 45 mg, 95% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.39 – 7.29 (m, 9H), 5.48 (d, J = 1.3 Hz, 1H), 5.43 (d, J = 1.2 Hz, 1H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ 150.9, 150.0, 141.9, 138.6, 128.5, 128.3, 128.0, 127.8, 125.2, 113.8, 34.7, 31.5.

MS (EI): Calcd for $\text{C}_{18}\text{H}_{20}$: 236.2; found: 236.1.



***m*-Hydroxy-1,1-diphenylethylene (3m) [51985-11-6].⁵**

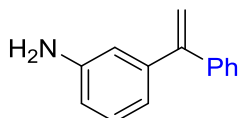
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 15:1 as eluent.

Colorless oil. 34 mg, 86% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.32 (m, 5H), 7.24 – 7.20 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.82 – 6.80 (m, 2H), 5.47 (s, 1H), 5.46 (s, 1H), 4.78 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 155.4, 149.8, 143.4, 141.4, 129.6, 128.4, 128.3, 127.9, 121.1, 115.4, 114.8, 114.7.

MS (EI): Calcd for C₁₄H₁₂O: 196.1; found: 196.1.



***m*-Amino-1,1-diphenylethylene (3n) [1610377-16-6].³**

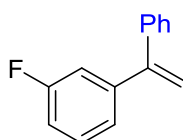
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 10:1 as eluent.

Colorless oil. 28 mg, 71% yield. When 1 equiv of phenylboroxine was used, the yield was increased to 83% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.30 (m, 5H), 7.16 – 7.12 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.66 – 6.65 (m, 2H), 5.45 (s, 1H), 5.43 (s, 1H), 3.63 (br s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 150.3, 146.3, 142.8, 141.7, 129.2, 128.5, 128.2, 127.7, 119.0, 115.2, 114.7, 114.1.

MS (EI): Calcd for C₁₄H₁₃N: 195.1; found: 195.1.



***m*-Fluoro-1,1-diphenylethylene (3o) [29265-80-3].⁶**

Colorless oil. 27 mg, 68% yield. When 1 equiv of phenylboroxine was used, the yield was increased to 82% after 24 h at 120 °C.

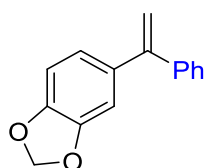
¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.23 (m, 6H), 7.12 – 7.10 (m, 1H), 7.06 – 6.98 (m, 2H), 5.478 (s, 1H),

5.475 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 162.9 (d, $J = 245.4$ Hz), 149.2 (d, $J = 1.9$ Hz), 143.9 (d, $J = 7.6$ Hz), 141.0, 129.7 (d, $J = 8.3$ Hz), 128.4 (d, $J = 5.4$ Hz), 128.1, 124.1 (d, $J = 2.9$ Hz), 115.3, 115.0 (d, $J = 38.6$ Hz), 115.0 (d, $J = 81.7$ Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ -113.6.

MS (EI): Calcd for $\text{C}_{14}\text{H}_{11}\text{F}$: 198.1; found: 198.1.



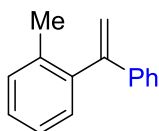
5-(1-Styryl)benzo[1,3]dioxole (3p) [51003-88-4].¹

Colorless oil. 32 mg, 71% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.32 (m, 5H), 6.84 – 6.77 (m, 3H), 5.97 (s, 2H), 5.39 (s, 1H), 5.36 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 149.8, 147.7, 147.4, 141.8, 135.9, 128.5, 128.3, 127.9, 122.2, 113.5, 108.8, 108.1, 101.2.

MS (EI): Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2$: 224.1; found: 224.1.



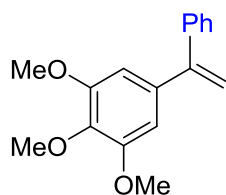
***o*-Methyl-1,1-diphenylethylene (3q) [947-77-3].¹**

Colorless oil. 34 mg, 88% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.33 – 7.17 (m, 9H), 5.77 (d, $J = 1.4$ Hz, 1H), 5.19 (d, $J = 1.3$ Hz, 1H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 149.7, 141.8, 140.8, 136.3, 130.23, 130.17, 128.5, 127.71, 127.67, 126.6, 125.8, 115.0, 20.2.

MS (EI): Calcd for $\text{C}_{15}\text{H}_{14}$: 194.1; found: 194.0.



3,4,5-Trimethoxy-1,1-diphenylethylene (3r) [1070196-63-2].⁷

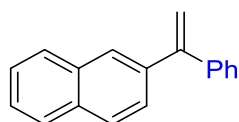
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 10:1 as eluent.

Colorless oil. 48 mg, 88% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.25 (m, 5H), 6.55 (s, 2H), 5.44 (s, 1H), 5.42 (s, 1H), 3.88 (s, 3H), 3.80 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 153.0, 150.2, 141.3, 137.9, 137.3, 128.3, 128.2, 127.9, 114.0, 105.8, 61.0, 56.2.

MS (EI): Calcd for C₁₇H₁₈O₃: 270.1; found: 270.1.



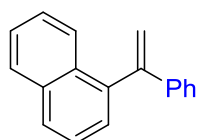
1-(2-Naphthyl)styrene (3s) [28358-66-9].¹

Colorless oil. 42 mg, 91% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.88 – 7.81 (m, 4H), 7.53 – 7.47 (m, 3H), 7.44 – 7.37 (m, 5H), 5.62 (d, *J* = 1.0 Hz, 1H), 5.58 (d, *J* = 1.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 150.2, 141.7, 139.1, 133.5, 133.1, 128.5, 128.4, 128.3, 127.9, 127.84, 127.75, 127.4, 126.6, 126.3, 126.2, 115.0.

MS (EI): Calcd for C₁₈H₁₄: 230.1; found: 230.1.



1-(1-Naphthyl)styrene (3t) [28358-65-8].¹

Colorless oil. 29 mg, 63% yield due to incomplete conversion of the ketone (69%).

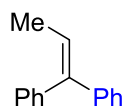
When 1 equiv of phenylboroxine was used, the yield was increased to 76% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 3.6 Hz, 1H), 7.84 (d, *J* = 3.6 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.34 – 7.30 (m, 3H), 7.28 – 7.24 (m, 3H), 5.98 (d, *J* = 1.2 Hz, 1H), 5.39 (d, *J*

= 1.2 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.5, 141.2, 140.0, 133.9, 132.0, 128.5, 128.3, 128.1, 127.9, 127.4, 126.8, 126.6, 126.0, 125.8, 125.6, 116.4.

MS (EI): Calcd for $\text{C}_{18}\text{H}_{14}$: 230.1; found: 230.2



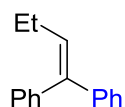
1,1-Diphenyl-1-propene (3u) [778-66-5].⁸

Colorless oil. 34 mg, 87% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.39 – 7.35 (m, 2H), 7.32 – 7.16 (m, 8H), 6.17 (q, J = 7.0 Hz, 1H), 1.76 (d, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.1, 142.6, 140.2, 130.2, 128.3, 128.2, 127.3, 127.0, 126.9, 124.3, 15.8.

MS (EI): Calcd for $\text{C}_{15}\text{H}_{14}$: 194.1; found: 194.1



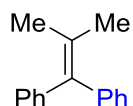
1,1-Diphenyl-1-butene (3v) [1726-14-3].⁹

Colorless oil. 34 mg, 81% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.37 – 7.17 (m, 10H), 6.07 (t, J = 7.5 Hz, 1H), 2.12 (vp, J = 7.5 Hz, 2H), 1.03 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.0, 141.1, 140.4, 131.9, 130.1, 128.3, 128.2, 127.4, 127.0, 126.9, 23.3, 14.7.

MS (EI): Calcd for $\text{C}_{16}\text{H}_{16}$: 208.1; found: 208.1.



1,1-diphenyl-1-isobutene (3w) [781-33-9].¹⁰

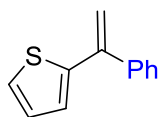
Yellow solid. 16 mg, 38% yield due to incomplete conversion of ketone (conversion: 43%).

When 1 equiv of phenylboroxine was used, the yield was increased to 58% after 24 h at 120 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.29 – 7.25 (m, 4H), 7.19 – 7.12 (m, 6H), 1.80 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.5, 137.3, 131.2, 130.0, 128.0, 126.2, 22.6.

MS (EI): Calcd for C₁₆H₁₆: 208.1; found: 208.1.



1-(2-Thienyl)styrene (3x) [30616-74-1].¹¹

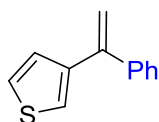
Colorless oil. 23 mg, 62% yield due to incomplete conversion of ketone (conversion: 83%).

When 1.0 equiv of phenylboroxine was used, the yield was increased to 76% after 24 h at 120 °C.

¹H NMR (300 MHz, CDCl₃): δ 7.45 – 7.33 (m, 5H), 7.23 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.91 (dd, *J* = 3.6, 1.0 Hz, 1H), 5.58 (s, 1H), 5.24 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 144.9, 143.5, 141.2, 128.5, 128.3, 128.2, 127.4, 126.6, 125.2, 113.8.

MS (EI): Calcd for C₁₂H₁₀S: 186.1; found: 186.0.



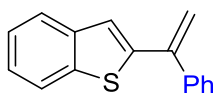
1-(3-Thienyl)styrene (3y) [75488-46-9].¹

Colorless oil. 25 mg, 66% yield. When 1.0 equiv of phenylboroxine was used, the yield was increased to 80% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.42 – 7.33 (m, 5H), 7.32 – 7.30 (m, 1H), 7.19 – 7.18 (m, 1H), 7.14 – 7.13 (m, 1H), 5.54 (s, 1H), 5.34 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 144.7, 142.7, 141.7, 128.3, 128.2, 127.9, 127.3, 125.6, 123.4, 113.6.

MS (EI): Calcd for C₁₂H₁₀S: 186.1; found: 186.0.



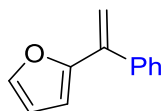
1-(2-benzothiienyl)styrene (3z).

Colorless oil. 39 mg, 82% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.82 – 7.77 (m, 1H), 7.67 – 7.63 (m, 1H), 7.50 – 7.47 (m, 2H), 7.44 – 7.39 (m, 3H), 7.34 – 7.30 (m, 2H), 7.08 (s, 1H), 5.72 (s, 1H), 5.39 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 144.9, 144.0, 140.7, 140.3, 139.6, 128.6, 128.4, 128.3, 124.9, 124.5, 123.9, 123.7, 122.2, 116.0.

MS (EI): Calcd for C₁₆H₁₂S: 236.1; found: 236.1.



1-(2-Furyl)styrene (3aa) [75488-41-4].¹¹

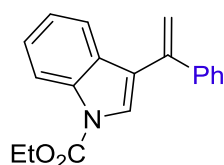
Colorless oil. 17 mg, 51% yield due to incomplete conversion of ketone (56%).

When 1.0 equiv. of phenylboroxine was used, the yield was increased to 75% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.48 – 7.43 (m, 3H), 7.41 – 7.34 (m, 3H), 6.40 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.21 (d, *J* = 3.3 Hz, 1H), 5.76 (d, *J* = 1.1 Hz, 1H), 5.24 (d, *J* = 1.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 154.3, 142.5, 139.8, 139.5, 128.5, 128.4, 128.2, 112.2, 111.4, 109.3.

MS (EI): Calcd for C₁₂H₁₀O: 170.1; found: 170.0.



N-Ethoxycarbonyl-1-(3-indolyl)styrene (3ab).

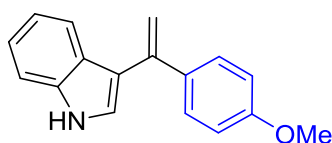
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent.

Yellow oil. 37 mg, 63% yield due to incomplete conversion of the ketone (66%). When 1 equiv of phenylboroxine was used, the yield was increased to 78% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.63 (s, 1H), 7.48 – 7.45 (m, 2H), 7.38 – 7.34 (m, 5H), 7.20 (t, *J* = 7.5 Hz, 1H), 5.63 (s, 1H), 5.62 (s, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 151.1, 141.9, 141.1, 135.9, 129.6, 128.4, 128.1, 127.9, 124.8, 124.6, 123.1, 122.8, 121.0, 115.4, 115.0, 63.4, 14.6.

MS (EI): Calcd for C₁₉H₁₇NO₂: 291.1; found: 291.1.



1-(3-Indolyl)-1-anisylethylene (3ac) [1646537-42-9].¹²

The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl

acetate 10:1 as eluent.

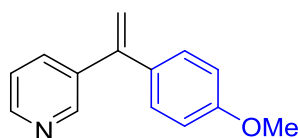
White solid. 22 mg, 45% yield with 64% conversion of ketone.

When 1 equiv of phenylboroxine was used, the yield was increased to 64% after 48 h at 110 °C.

¹H NMR (400 MHz, *d*₄-MeOD): δ 7.38 – 7.33 (m, 4H), 7.13 (s, 1H), 7.11 – 7.07 (m, 1H), 6.97 – 6.93 (m, 1H), 6.89 – 6.85 (m, 2H), 5.40 (d, *J* = 1.9 Hz, 1H), 5.25 (d, *J* = 1.9 Hz, 1H), 3.80 (s, 3H).

¹³C NMR (100 MHz, *d*₄-MeOD): δ 159.4, 143.6, 137.1, 135.2, 128.8, 126.2, 124.4, 121.1, 119.9, 118.8, 117.0, 113.0, 111.0, 108.6, 54.3.

MS (EI): Calcd for C₁₇H₁₅NO: 249.1; found: 249.1.



1-Anisoyl-1-(3-pyridyl)ethylene (3ad).

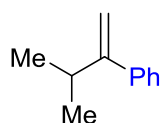
The reaction was stirred at 130 °C for 2 days, and the desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 5:1 as eluent.

Colorless oil. 33 mg, 78% yield.

¹H NMR (400 MHz, CDCl₃): δ 8.63 (d, *J* = 1.8 Hz, 1H), 8.56 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.27 – 7.24 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.50 (s, 1H), 5.39 (s, 1H), 3.83 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 159.8, 149.5, 149.0, 146.5, 137.5, 135.7, 133.0, 129.3, 123.1, 114.5, 113.9, 55.5.

MS (EI): Calcd for C₁₄H₁₃NO: 211.1; found: 211.1.



1-Isopropylstyrene (3af) [17498-71-4].¹³

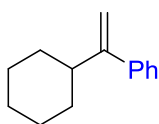
The 2 isomers in the mixture were determined to be 8:1 by GC. 2 isomers were separated on silica. Colorless oil.

22 mg, 75% yield of the major isomer.

¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 5.14 (s, 1H), 5.03 (s, 1H), 2.83 (hept, *J* = 6.7 Hz, 1H), 1.10 (d, *J* = 6.8 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 156.0, 143.0, 128.3, 127.2, 126.8, 110.1, 32.5, 22.2.

MS (EI): Calcd for C₁₁H₁₄: 146.1; found: 146.0.



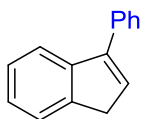
1-Cyclohexylstyrene (3ag) [5700-44-7].¹⁴

Only one isomer was detected in the mixture by GC. Colorless oil. 26 mg, 68% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.35 – 7.23 (m, 5H), 5.13 (d, *J* = 0.9 Hz, 1H), 5.00 (dd, *J* = 1.3, 1.3 Hz, 1H), 2.42 (t, *J* = 11.3 Hz, 1H), 1.86 – 1.76 (m, 4H), 1.73 – 1.70 (m, 1H), 1.38 – 1.30 (m, 2H), 1.21 – 1.12 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 155.2, 143.2, 128.3, 127.1, 126.8, 110.5, 42.8, 32.9, 27.0, 26.6.

MS (EI): Calcd for C₁₄H₁₈: 186.1; found: 186.1.



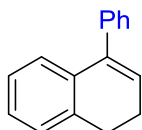
1-Phenyl-1-indene (3ah) [1961-97-3].¹⁵

Colorless oil. 26 mg, 68% yield. When 1.0 equiv of phenylboroxine was used, the yield was increased to 87% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.61 – 7.58 (m, 3H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.45 (ψt, *J* = 7.4 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.32 (ψt, *J* = 7.4 Hz, 1H), 7.27 – 7.24 (m, 1H), 6.58 (t, *J* = 2.1 Hz, 1H), 3.51 (d, *J* = 1.9 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 145.4, 144.9, 144.1, 136.3, 131.1, 128.7, 127.9, 127.7, 126.3, 125.0, 124.3, 120.5, 38.3.

MS (EI): Calcd for C₁₅H₁₂: 192.1; found: 192.1.



4-Phenyl-1,2-dihydronaphthalene (3ai) [7469-40-1].⁴

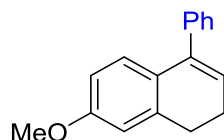
Colorless oil. 25 mg, 61% yield. When 1.0 equiv of phenylboroxine was used, the yield was increased to 85% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.41 – 7.31 (m, 5H), 7.23 – 7.21 (m, 1H), 7.19 – 7.15 (m, 1H), 7.14 – 7.10 (m, 1H), 7.03 – 7.01 (m, 1H), 6.10 (t, *J* = 4.7 Hz, 1H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.45 – 2.40 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 141.0, 140.1, 136.9, 135.3, 128.9, 128.4, 127.8, 127.7, 127.2, 127.1, 126.3, 125.6,

28.5, 23.7.

MS (EI): Calcd for C₁₆H₁₄: 206.1; found: 206.1.



7-Methoxy-4-phenyl-1,2-dihydronaphthalene (3aj) [2844-82-8].¹⁶

The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent.

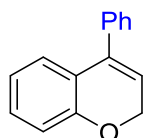
Colorless oil. 26 mg, 56% yield due to incomplete conversion of ketone (62%).

When 1.0 equiv of phenylboroxine was used, the yield was increased to 77% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.39 – 7.30 (m, 5H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.65 – 6.62 (m, 1H), 5.96 (t, *J* = 4.7 Hz, 1H), 3.81 (s, 3H), 2.84 (t, *J* = 7.9 Hz, 2H), 2.42 – 2.37 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 158.7, 141.2, 139.6, 138.8, 128.9, 128.4, 128.3, 127.2, 126.8, 125.3, 113.9, 110.9, 55.4, 29.0, 23.7.

MS (EI): Calcd for C₁₇H₁₆O: 236.1; found: 236.1.



4-Phenyl-2-chromene (3ak) [51870-64-5].¹⁷

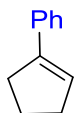
Colorless oil. 25 mg, 60% yield due to incomplete conversion of ketone (65%).

When 1.0 equiv of phenylboroxine was used, the yield was increased to 78% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.42 – 7.33 (m, 5H), 7.18 – 7.14 (m, 1H), 7.02 – 6.99 (m, 1H), 6.91 – 6.89 (m, 1H), 6.87 – 6.83 (m, 1H), 5.80 (t, *J* = 3.9 Hz, 1H), 4.86 (d, *J* = 4.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 154.9, 138.5, 137.3, 129.4, 128.8, 128.5, 127.9, 126.0, 123.9, 121.3, 120.1, 116.4, 65.4.

MS (EI): Calcd for C₁₅H₁₂O: 208.1; found: 208.0.



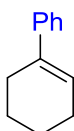
1-Phenylcyclopentene (3al) [825-54-7].¹⁸

Colorless oil. 21 mg, 74% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.46 – 7.43 (m, 2H), 7.33 – 7.29 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.20 – 6.18 (m, 1H), 2.75 – 2.69 (m, 2H), 2.56 – 2.51 (m, 2H), 2.06 – 1.99 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 142.6, 137.0, 128.4, 127.0, 126.2, 125.7, 33.5, 33.3, 23.5.

MS (EI): Calcd for C₁₁H₁₂: 144.1; found: 144.1.



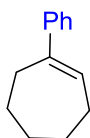
1-Phenylcyclohexene (3am) [771-98-2].¹⁸

Colorless oil. 28 mg, 89% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.38 (m, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.19 (m, 1H), 6.14 – 6.11 (m, 1H), 2.45 – 2.40 (m, 2H), 2.25 – 2.19 (m, 2H), 1.83 – 1.77 (m, 2H), 1.70 – 1.65 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 142.9, 136.8, 128.3, 126.7, 125.1, 124.9, 27.6, 26.0, 23.2, 22.3.

MS (EI): Calcd for C₁₂H₁₄: 158.1; found: 158.1.



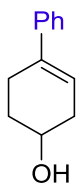
1-Phenylcycloheptene (3an) [25308-75-2].¹⁸

Colorless oil. 25 mg, 72% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.34 – 7.26 (m, 4H), 7.22 – 7.16 (m, 1H), 6.09 (t, *J* = 6.8 Hz, 1H), 2.63 – 2.59 (m, 2H), 2.32 – 2.26 (m, 2H), 1.88 – 1.80 (m, 2H), 1.68 – 1.61 (m, 2H), 1.59 – 1.52 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 145.2, 145.1, 130.6, 128.3, 126.4, 125.8, 32.94, 32.92, 29.0, 27.1, 27.0.

MS (EI): Calcd for C₁₃H₁₆: 172.1; found: 172.1.



4-Hydroxy-1-phenylcyclohexene (3ao) [15619-51-9].¹⁹

The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 3:1 as eluent.

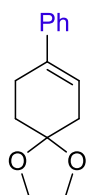
White solid. 17 mg, 49% yield due to incomplete conversion of the carbinol and no dehydration of alcohol group in the reactant was detected by GCMS.

When 1.0 equiv of phenylboroxine was used, the yield was increased to 90% after 24 h at 120 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.00 – 5.98 (m, 1H), 4.08 – 4.02 (m, 1H), 2.64 – 2.47 (m, 3H), 2.25 – 2.17 (m, 1H), 2.05 – 1.98 (m, 1H), 1.86 – 1.77 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 141.7, 136.5, 128.4, 127.0, 125.2, 121.5, 66.7, 35.0, 31.3, 25.7.

MS (EI): Calcd for C₁₂H₁₄O: 174.1; found: 174.0.



4-Phenylcyclohex-3-en-1-one ethylene glycol ketal (3ap) [724707-89-5].²⁰

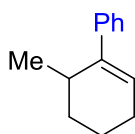
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent.

Yellow oil. 30 mg, 69% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.30 (ψt, *J* = 7.5 Hz, 2H), 7.22 (ψt, *J* = 7.2 Hz, 1H), 6.00 – 5.98 (m, 1H), 4.03 (s, 4H), 2.69 – 2.66 (m, 2H), 2.48 (s, 2H), 1.93 (t, *J* = 6.5 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 141.6, 136.4, 128.3, 127.0, 125.4, 121.7, 107.9, 64.6, 36.3, 31.5, 26.9.

MS (EI): Calcd for C₁₄H₁₆O₂: 216.1; found: 216.0.



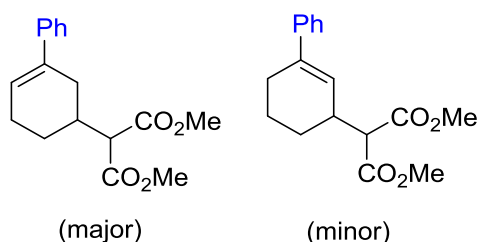
6-Methyl-1-phenylcyclohexene (3aq) [92020-20-7].²¹

2 isomers were detected in the reaction mixture (9:1 by GC). Colorless oil. 27 mg, 78% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.32 – 7.26 (m, 4H), 7.22 – 7.12 (m, 1H), 5.87 (td, *J* = 4.0, 1.2 Hz, 1H), 2.85 – 2.80 (m, 1H), 2.18 – 2.14 (m, 2H), 1.91 – 1.84 (m, 1H), 1.75 – 1.68 (m, 1H), 1.66 – 1.56 (m, 2H), 0.93 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 143.1, 142.9, 128.3, 126.5, 126.4, 125.6, 31.2, 30.6, 26.4, 20.4, 19.1.

MS (EI): Calcd for C₁₃H₁₆: 172.1; found: 172.1.



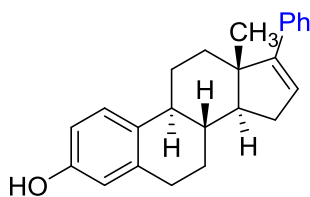
Dimethyl 2-(1-phenylcyclohex-1-en-5-yl)malonate (major) (3ar) and dimethyl 2-(1-phenylcyclohex-1-en-3-yl)-malonate (minor) (3ar')

The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 10:1 as eluent. Colorless oil. 39 mg, 67% yield (a mixture of 2 isomers). When 1.0 equiv of phenylboroxine was used, the yield was increased to 93% after 30 h at 120 °C. The ratio in the crude mixture was determined by GC (1.8:1). The two isomers are inseparable on silica and the ratio of 2 isomers in a crude mixture was determined by GC (1.8:1). The structure of the minor isomer is assigned by comparison with literature NMR data.²²

¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.27 (m, 4H+2.33H, major+minor), 7.25 – 7.19 (m, 1H+0.58H, major+minor), 6.09 (br s, 1H, major), 5.92 (br s, 0.57H, minor), 3.76 – 3.74 (m, 6H+3.55H, major+minor), 3.40 (d, *J* = 8.8 Hz, 1H, major), 3.38 (d, *J* = 9.2 Hz, 0.56H, minor), 3.13 – 3.07 (m, 0.58H, minor), 2.59 – 2.50 (m, 2H, major), 2.42 – 2.40 (m, 1.16H, minor), 2.31 – 2.24 (m, 3H, major), 1.92 – 1.81 (m, 1H+1.24H, major+minor), 1.77 – 1.67 (m, 0.61H, minor), 1.46 – 1.37 (m, 1H+0.60H, major+minor).

¹³C NMR (100 MHz, CDCl₃): δ 169.2, 169.1, 169.0, 168.9, 142.2, 142.1, 139.4, 135.4, 128.3, 127.2, 126.9, 125.4, 125.2, 124.8, 124.3, 57.1, 57.0, 52.6, 52.5, 36.2, 34.5, 31.6, 27.5, 26.4, 26.2, 25.5, 21.6.

MS (EI): Calcd for C₁₇H₂₀O₄: 288.1; found: 288.1.



(8*S*,9*S*,13*S*,14*S*)-13-Methyl-17-phenyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-3-ol (3as) [1235454-72-4].⁴

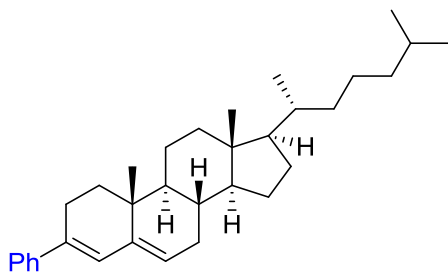
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 10:1 as the eluent.

White solid. 42 mg, 63% yield of a single isomer from 3-estrone.

¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 5.94 (dd, *J* = 3.0, 1.7 Hz, 1H), 4.57 (s, 1H), 2.96 – 2.82 (m, 2H), 2.38 – 2.27 (m, 3H), 2.22 – 2.19 (m, 1H), 2.16 – 2.08 (m, 1H), 1.99 – 1.94 (m, 1H), 1.84 – 1.77 (m, 1H), 1.72 – 1.62 (m, 3H), 1.53 – 1.42 (m, 1H), 1.07 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 155.2, 153.5, 138.5, 137.5, 133.2, 128.3, 127.2, 126.91, 126.88, 126.4, 115.4, 112.8, 57.0, 47.8, 44.3, 37.5, 35.7, 31.5, 29.7, 27.8, 26.8, 16.9.

MS (ESI): Calcd for C₂₄H₂₆O [M+H]⁺: 331.2; found: 331.4.



3-Phenyl-3,5-cholestadiene (3at) [2309-35-5].²³

The two isomers were inseparable on silica gel and the pure major isomer was obtained by crystallization from a solution in hot hexanes.

White solid. 71 mg, 79% yield of a mixture of 2 isomers (5:1) based on proton NMR spectroscopy.

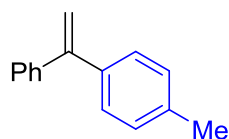
¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.44 (s, 1H), 5.58 (s, 1H), 2.55 – 2.54 (m, 2H), 2.25 (dt, *J* = 17.7, 4.5 Hz, 1H), 2.07 – 1.97 (m, 2H), 1.89 – 1.81 (m, 1H), 1.78 – 1.60 (m, 4H), 1.53 – 1.44 (m, 2H), 1.42 – 1.24 (m, 6H), 1.22 – 1.02 (m, 9H), 1.00 (s, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 1.5 Hz, 3H), 0.86 (d, *J* = 1.4 Hz, 3H), 0.72 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 142.4, 141.5, 133.5, 128.4, 126.8, 126.3, 125.1, 125.0, 57.1, 56.4, 48.5, 42.7, 40.0,

39.7, 36.4, 36.0, 35.0, 34.4, 32.3, 32.0, 28.4, 28.2, 24.8, 24.4, 24.0, 23.0, 22.7, 21.3, 19.3, 18.9, 12.2.

MS (ESI) Calcd for C₂₃H₄₈ [M+H]⁺: 445.4; found: 445.2.

(2) Examples of nickel-catalyzed arylation of other arylboroxines



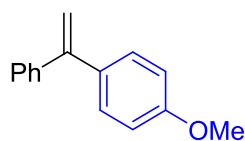
***p*-Methyl-1,1-diphenylethylene (3au) [948-55-0].¹**

Colorless oil. 30 mg, 78% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.29 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 5.43 (d, *J* = 1.1 Hz, 1H), 5.40 (d, *J* = 1.2 Hz, 1H), 2.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 150.1, 141.9, 138.8, 137.7, 129.0, 128.4, 128.30, 128.26, 127.8, 113.8, 21.3.

MS (EI): Calcd for C₁₅H₁₄: 194.1; found: 194.1.



***p*-Methoxy-1,1-diphenylethene (3av) [4333-75-9].¹**

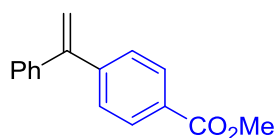
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent.

White solid. 35 mg, 82% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.32 (m, 5H), 7.32 – 7.28 (m, 2H), 6.90 – 6.86 (m, 2H), 5.41 (d, *J* = 1.2 Hz, 1H), 5.37 (d, *J* = 1.2 Hz, 1H), 3.84 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 159.5, 149.7, 142.0, 134.2, 129.5, 128.5, 128.3, 127.8, 113.7, 113.1, 55.4.

MS (EI): Calcd for C₁₅H₁₄O: 210.1; found: 210.0.



***p*-Methoxycarbonyl-1,1-diphenylethylene (3aw) [29265-82-5].²⁴**

The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl

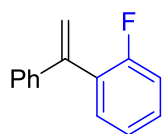
acetate 15:1 as eluent.

White solid. 25 mg, 52% yield after 48 h at 120 °C, the low yield was due to incomplete conversion of ketone (61%).

^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.36 – 7.30 (m, 5H), 5.55 (s, 1H), 5.54 (s, 1H), 3.93 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 167.1, 149.5, 146.2, 141.0, 129.7, 129.5, 128.5, 128.37, 128.35, 128.1, 116.0, 52.2.

MS (EI): Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2$: 238.1; found: 238.1.



***o*-Fluoro-1,1-diphenylethylene (3ax) [389-42-4].²⁵**

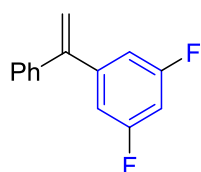
Colorless oil. 36 mg, 90% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.26 (m, 7H), 7.14 (td, J = 7.5, 1.2 Hz, 1H), 7.09 – 7.04 (m, 1H), 5.75 (s, 1H), 5.42 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 160.3 (d, J = 248.4 Hz), 144.4, 140.7, 131.7 (d, J = 3.7 Hz), 129.54, 129.46, 128.4, 127.9, 127.0, 124.1 (d, J = 3.7 Hz), 117.1 (d, J = 1.7 Hz), 115.9 (d, J = 22.3 Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ -113.2.

MS (EI): Calcd for $\text{C}_{14}\text{H}_{11}\text{F}$: 198.1; found: 198.0.



***m,m*-Difluoro-1,1-diphenylethylene (3ay).**

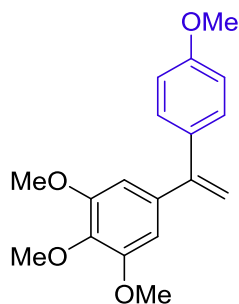
Colorless oil. 31 mg, 71% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.38 – 7.33 (m, 3H), 7.32 – 7.29 (m, 2H), 6.89 – 6.83 (m, 2H), 6.76 (tt, J = 8.8, 2.3 Hz, 1H), 5.51 (s, 1H), 5.50 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 163.0 (dd, J = 247.9, 12.9 Hz), 148.5, 145.0, 140.4, 128.6, 128.4, 116.1, 111.3 (d, J = 25.5 Hz), 111.3 (d, J = 11.6 Hz), 103.2 (dd, J = 25.4, 25.4 Hz).

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ -110.4.

MS (EI): Calcd for $\text{C}_{14}\text{H}_{10}\text{F}_2$: 216.1; found: 216.0.



***m,m,p,p'*-Tetramethoxy-1,1-diphenylethylene (3az) [1067880-32-3].⁷**

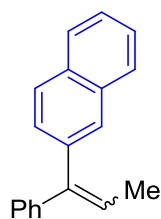
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 10:1 as eluent.

Colorless oil. 45 mg, 75% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.30 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.56 (s, 2H), 5.37 (d, J = 0.9 Hz, 1H), 5.32 (d, J = 0.9 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.81 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 159.5, 153.0, 149.6, 137.9, 137.7, 133.8, 129.5, 113.6, 112.6, 105.8, 61.0, 56.2, 55.4.

MS (EI): Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4$: 300.1; found: 300.1.



1-(2-Naphthyl)-1-phenyl-1-propene (3ba and 3ba').

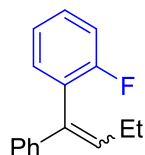
Colorless oil. 35 mg, 72% yield. The two E/Z isomers were inseparable on silica gel and the ratio in the crude mixture was determined by GC (1:1).

NMR for a mixture of two isomers:

^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.68 (m, 7H), 7.55 (br s, 1H), 7.49 – 7.45 (m, 2H), 7.43 – 7.37 (m, 5H), 7.34 – 7.30 (m, 1H), 7.27 (dd, J = 8.4, 1.6 Hz, 1H), 7.25 – 7.19 (m, 7H), 6.31 (q, J = 7.0 Hz, 1H), 6.26 (q, J = 7.0 Hz, 1H), 1.81 (s, 3H), 1.80 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.0, 142.6, 142.5, 140.5, 140.1, 137.7, 133.54, 133.50, 132.61, 132.59, 130.3, 129.0, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.1, 127.0, 126.3, 126.14, 126.12, 126.0, 125.7, 125.6, 124.9, 124.7, 16.0, 15.9.

MS (EI): Calcd for $\text{C}_{19}\text{H}_{16}$: 244.1; found: 244.1.



1-*o*-Fluorophenyl-1-phenyl-1-propenes (3bb and 3bb').

Light yellow oil. 24 mg, 53% yield due to incomplete conversion of butyrophenone (89%) and incomplete elimination of the carbinol. No other byproducts were detected in GC and GCMS.

When 1 equiv of phenylboroxine was used, the yield was increased to 92% after 24 h at 120 °C, and the ratio in the crude mixture was determined by GC (1.8:1).

The two isomers were inseparable on silica gel and the ratio in the crude mixture was determined by GC (2:1).

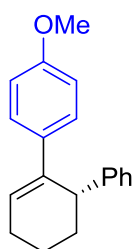
NMR for a mixture of two isomers:

^1H NMR (400 MHz, CDCl_3): δ 7.39 – 7.13 (m, 23H), 7.13 – 7.07 (m, 2H), 7.04 (t, $J = 7.5$ Hz, 1H), 7.01 – 6.94 (m, 1H), 6.23 (t, $J = 7.5$ Hz, 2H), 5.97 (t, $J = 7.5$ Hz, 1H), 2.22 (vp, $J = 7.5$ Hz, 2H), 2.04 (vp, $J = 7.5$ Hz, 4H), 1.11 – 0.96 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ 160.4 (d, $J = 246.6$ Hz), 160.3 (d, $J = 244.3$ Hz), 141.6, 140.3, 135.9 (d, $J = 3.2$ Hz), 135.7, 134.7, 133.8, 132.2 (d, $J = 4.1$ Hz), 131.6, 131.4 (d, $J = 3.6$ Hz), 130.1, 129.4, 129.2 (d, $J = 8.0$ Hz), 128.5 (d, $J = 8.1$ Hz), 128.4, 128.3 (d, $J = 6.6$ Hz), 128.1, 127.7, 127.5, 127.4, 127.1, 127.0, 126.6, 124.1 (d, $J = 3.4$ Hz), 123.8 (d, $J = 3.6$ Hz), 115.9 (d, $J = 22.7$ Hz), 115.8 (d, $J = 22.3$ Hz), 23.6, 23.1, 14.6, 14.1.

^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ -114.1, -114.4.

MS (EI): Calcd for $\text{C}_{16}\text{H}_{15}\text{F}$: 226.1; found: 226.1.



6-Phenyl-1-anisoylcyclohexene (3bc).

White solid. 44 mg, 84% yield. 71% ee from a starting material of 73% ee. The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent. Only a single olefinic isomer was detected by GCMS.

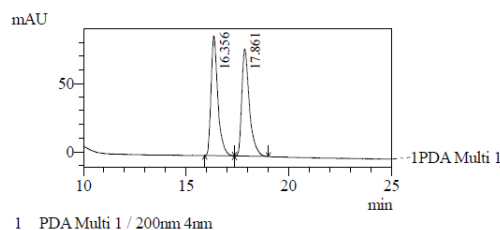
$[\alpha]_D^{20} = 103.9^\circ$ ($c = 0.81$, CHCl_3) for a sample of 71% ee.

^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.19 (m, 6H), 7.14 – 7.09 (m, 1H), 6.71 (dd, $J = 11.7, 2.9$ Hz, 2H), 6.31 (t, $J = 3.9$ Hz, 1H), 3.97 (br s, 1H), 3.71 (s, 3H), 2.36 – 2.22 (m, 2H), 2.11 – 2.02 (m, 1H), 1.87 – 1.81 (m, 2H), 1.57 – 1.51 (m, 2H).

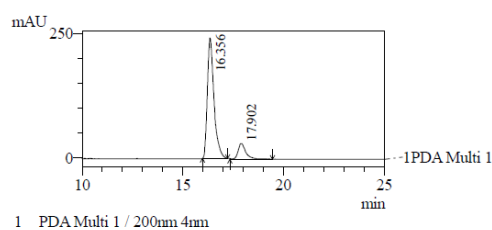
^{13}C NMR (100 MHz, CDCl_3): δ 158.3, 145.4, 137.2, 134.6, 128.7, 128.2, 126.9, 126.4, 125.9, 113.6, 55.3, 42.7, 32.8, 26.2, 17.5.

MS (EI): Calcd for $\text{C}_{19}\text{H}_{20}\text{O}$: 264.2; found: 264.1.

The ee of 2-phenylcyclohexanone was determined to be 73% by chiral HPLC analysis (Daicel CHIRALCEL OD-H; hexanes: *i*-PrOH = 95:5; detection wavelengths = 200 nm; flow rate = 0.5 mL/min). $T_R = 16.4$ min (major) and 17.9 min (minor).

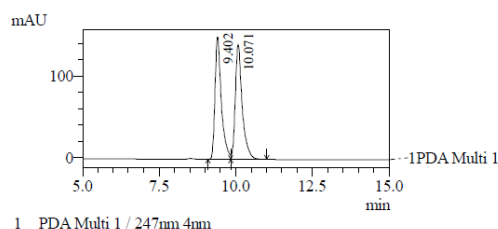


PeakTable			
PDA Ch1 200nm 4nm			
Peak#	Ret. Time	Area	Area %
1	16.356	2001051	49.988
2	17.861	2002015	50.012
Total		4003066	100.000

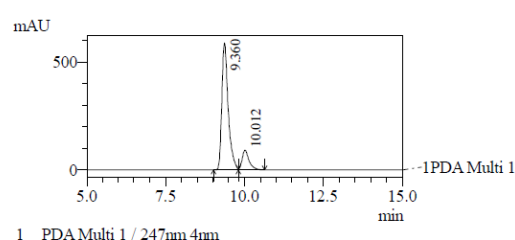


PeakTable			
PDA Ch1 200nm 4nm			
Peak#	Ret. Time	Area	Area %
1	16.356	5483942	86.451
2	17.902	859449	13.549
Total		6343391	100.000

The ee of the olefin product was determined to be 71% by chiral HPLC analysis (Daicel CHIRALCEL OD-H; hexanes: *i*-PrOH = 98:2; detection wavelengths = 247 nm; flow rate = 0.5 mL/min). $T_R = 9.4$ min (major) and 10.0 min (minor).



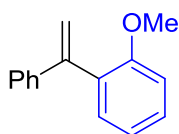
PeakTable			
PDA Ch1 247nm 4nm			
Peak#	Ret. Time	Area	Area %
1	9.402	2153567	49.534
2	10.071	2194059	50.466
Total		4347626	100.000



PeakTable			
PDA Ch1 247nm 4nm			
Peak#	Ret. Time	Area	Area %
1	9.360	8346939	85.454
2	10.012	1420830	14.546
Total		9767769	100.000

(3) Nickel-catalyzed arylation using arylboronic acids

A typical procedure: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with $\text{Ni}(\text{PPh}_3)_4$ (5 mol%, 11 mg, 0.01 mmol), 1,2-bis(dicyclohexylphosphino)ethane (6 mol%, 5 mg, 0.012 mmol) and 2 mL of dry toluene. After stirring at room temperature for 5 minutes, acetophenone (24 mg, 0.2 mmol), phenylboronic acid (37 mg, 0.3 mmol), dry 5 Å molecular sieves (200 mg) and GC standard *n*-dodecane (20 µL) were then added sequentially. The tube was capped tightly and the reaction mixture was heated in an oil bath maintained at 120 °C for 1 day. The desired products were purified by flash chromatography over silica gel using hexanes as the elute. Similar results were obtained when the reactions were set up with a standard vacuum manifold and Schlenk tube. 5 Å molecular sieve was purchased from Alfa Aesar (catalog L05722; lot 10152947) and was grounded with pestle and mortar. The MS powder was then dried in a vacuum oven at 150 °C overnight and stored in an argon-filled glove box.



***o*-Methoxy-1,1-diphenylethene (3bd) [24892-80-6].²⁶**

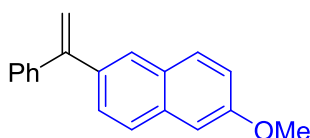
The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl acetate 20:1 as eluent.

Colorless oil. 22 mg, 51% yield due to incomplete conversion of acetophenone (59%).

¹H NMR (400 MHz, CDCl_3): δ 7.35 – 7.23 (m, 7H), 6.98 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 5.73 (s, 1H), 5.32 (s, 1H), 3.63 (s, 3H).

¹³C NMR (100 MHz, CDCl_3): δ 157.2, 147.1, 141.2, 131.4, 131.3, 129.1, 128.2, 127.4, 126.5, 120.7, 115.5, 111.4, 55.7.

MS (EI): Calcd for $\text{C}_{15}\text{H}_{14}\text{O}$: 210.1; found: 210.0.



2-Methoxy-6-(1-styryl)naphthalene (3be).

The desired product was purified by flash chromatography over silica gel using a mixture of hexanes and ethyl

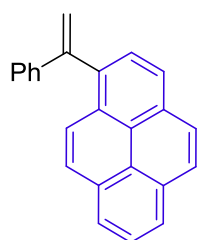
acetate 20:1 as eluent.

Colorless oil. 40 mg, 77% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.73 – 7.69 (m, 3H), 7.48 (dd, J = 8.5, 1.8 Hz, 1H), 7.43 – 7.36 (m, 5H), 7.18 – 7.15 (m, 2H), 5.59 (d, J = 1.0 Hz, 1H), 5.52 (d, J = 1.0 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 158.0, 150.2, 141.9, 136.8, 134.3, 129.8, 128.9, 128.6, 128.3, 127.9, 127.2, 127.0, 126.7, 119.1, 114.3, 105.8, 55.5.

MS (EI): Calcd for $\text{C}_{19}\text{H}_{16}\text{O}$: 260.1; found: 260.1.



1-(1-Styryl)pyrene (3bf).

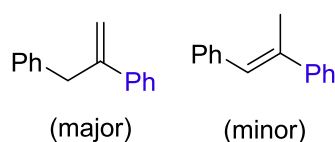
White solid, 24 mg, 40% yield due to incomplete conversion of acetophenone (43%).

^1H NMR (400 MHz, CDCl_3): δ 8.18 (d, J = 4.0 Hz, 1H), 8.16 (d, J = 3.8 Hz, 1H), 8.12 (d, J = 7.2 Hz, 1H), 8.08 – 8.05 (m, 3H), 7.98 (t, J = 7.6 Hz, 1H), 7.94 (d, J = 3.2 Hz, 1H), 7.92 (d, J = 1.8 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.28 – 7.23 (m, 3H), 6.14 (d, J = 1.2 Hz, 1H), 5.49 (d, J = 1.2 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.6, 141.6, 137.5, 131.5, 131.1, 131.0, 129.3, 128.6, 127.93, 127.92, 127.54, 127.48, 127.0, 126.1, 125.8, 125.3, 125.14, 125.06, 125.0, 124.8, 117.1.

MS (EI): Calcd for $\text{C}_{24}\text{H}_{16}$: 304.1; found: 304.1.

(4) Other examples of nickel-catalyzed arylation reaction of unsymmetrical ketones



1-Benzylstyrene (3bg) [948-97-0]²⁷ and (*E*)-1-methylstilbene (3bg') [833-81-8].²⁸

The two isomers were separated on silica gel and the ratio of the crude mixture was determined by GC (1.8:1).

The structures of the isomers were assigned by comparison with literature NMR data.

34 mg, 89% yield (combined yield of 2 isomers).

1-Benzylstyrene (3bg) (major). Colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.41 (m, 2H), 7.31 – 7.22 (m, 7H), 7.20 – 7.16 (m, 1H), 5.49 (s, 1H), 5.02 (d, *J* = 1.3 Hz, 1H), 3.84 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 147.1, 141.0, 139.7, 129.1, 128.5, 128.4, 127.6, 126.3, 126.2, 114.7, 41.8.

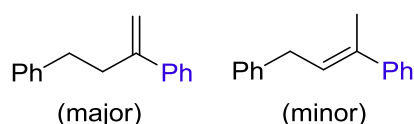
MS (EI): Calcd for C₁₅H₁₄: 194.1; found: 194.1.

(*E*)-1-Methylstilbene (3bg') (minor). White solid.

¹H NMR (400 MHz, CDCl₃): δ 7.54 – 7.52 (m, 2H), 7.39 – 7.35 (m, 6H), 7.31 – 7.22 (m, 2H), 6.84 (br, 1H), 2.29 (d, *J* = 1.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 144.1, 138.5, 137.6, 129.3, 128.5, 128.3, 127.9, 127.3, 126.6, 126.2, 17.6.

MS (EI): Calcd for C₁₅H₁₄: 194.1; found: 194.1.



1-(2-Phenylethyl)styrene (major) (3bh) [16606-47-6]²⁹ and (*E*)-2-benzylmethastylene (minor) (3bh') [14212-46-5].³⁰

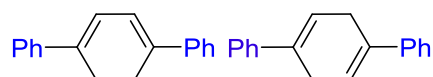
34 mg, 82% combined yield. The two isomers are inseparable on silica gel and the ratio of the crude mixture was determined by GC (1.9:1). The structures of isomers were assigned by comparing with literature NMR data.

NMR for a mixture of two isomers:

¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.40 (m, 5H), 7.36 – 7.17 (m, 20H), 5.97 (td, *J* = 7.4, 1.3 Hz, 1H), 5.29 (s, 1.4H), 5.06 (d, *J* = 1.0 Hz, 1.4H), 3.57 (d, *J* = 7.4 Hz, 2H), 2.84 – 2.77 (m, 5H), 2.14 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 148.0, 143.8, 142.1, 141.3, 141.2, 135.9, 128.63, 128.58, 128.55, 128.50, 128.46, 128.3, 127.6, 126.9, 126.3, 126.1, 126.0, 125.9, 112.8, 37.4, 35.1, 34.9, 16.1.

MS (EI): Calcd for C₁₆H₁₆: 208.1; found: 208.1.



1,4-Diphenylcyclohexa-1,3-diene (3bi) [21113- 62-2] and 1,4-diphenylcyclohexa-1,4-diene (3bi') [66241-48-3].

1 equiv of (PhBO)₃ was used. Yellow solid. 40 mg, 85% yield (combined yield).

The two isomers were inseparable on silica gel and the ratio in a crude mixture was determined by GC (1:1).

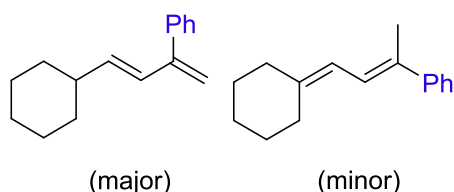
The structure of the conjugated 1,3-diene was assigned by comparison with literature NMR data.³¹

NMR for a mixture of two isomers:

^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, $J = 7.7$ Hz, 4H), 7.46 (d, $J = 7.6$ Hz, 4H), 7.35 (t, $J = 7.6$ Hz, 8H), 7.28–7.22 (m, 4H), 6.52 (s, 2H), 6.27 (s, 2H), 3.30 (s, 4H), 2.78 (s, 4H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.2, 140.8, 136.1, 133.4, 128.6, 128.5, 127.21, 127.18, 125.2, 125.1, 121.78, 121.77, 29.6, 26.3.

MS (EI): Calcd for $\text{C}_{18}\text{H}_{16}$: 232.1; found: 232.1.



(E)-1-Cyclohexyl-3-phenyl-1,3-butadiene (major) (3bj) and (E)-(4-cyclohexylidenebut-2-en-2-yl)benzene (minor) (3bj').

18 mg, 41% yield for two isomers due to incomplete conversion of ketone (62%). The ratio in the crude mixture was determined by GC (2.1:1). When 1 equiv of phenylboroxine and $\text{Ni}(\text{PPh}_3)_4$ (5 mol%), dcype (6 mol%) were used, the yield was increased to 68% after 30 h at 110 °C.

When 1 equiv of phenylboroxine and $\text{Ni}(\text{PPh}_3)_4$ (10 mol%), dcype (12 mol%) were used, the yield was increased to 83% after 30 h at 110 °C. The ratio in the crude mixture was determined by GC (2.2:1).

(E)-1-Cyclohexyl-3-phenyl-1,3-butadiene (3bj). Colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.25 (m, 5H), 6.26 (d, $J = 15.8$ Hz, 1H), 5.61 (dd, $J = 15.8, 7.0$ Hz, 1H), 5.18 (d, $J = 1.3$ Hz, 1H), 5.06 (d, $J = 1.8$ Hz, 1H), 2.07 – 2.00 (m, 1H), 1.74 – 1.70 (m, 4H), 1.66 – 1.63 (m, 1H), 1.33 – 1.28 (m, 1H), 1.23 – 1.03 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.4, 140.9, 140.3, 128.9, 128.4, 128.2, 127.4, 114.7, 41.2, 32.9, 26.3, 26.2.

MS (EI): Calcd for $\text{C}_{16}\text{H}_{20}$: 212.2; found: 212.1.

(E)-(4-Cyclohexylidenebut-2-en-2-yl)benzene (3bj'). Colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.44 (d, $J = 7.4$ Hz, 2H), 7.32 (ψt , $J = 7.7$ Hz, 2H), 7.22 (ψt , $J = 7.3$ Hz, 1H), 6.68 (d, $J = 11.4$ Hz, 1H), 6.15 (d, $J = 11.4$ Hz, 1H), 2.39 – 2.37 (m, 2H), 2.25 – 2.23 (m, 2H), 2.16 (s, 3H), 1.59 (br s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 144.8, 144.3, 133.8, 128.4, 126.7, 125.7, 122.9, 118.9, 38.1, 29.5, 28.9, 28.0, 27.0, 15.9.

MS (EI): Calcd for $C_{16}H_{20}$: 212.2; found: 212.1.

IV. Mechanistic studies

(1) Kinetic studies of entire catalytic reactions

A typical procedure: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with $\text{Ni}(\text{PPh}_3)_4$ (5 mol%, 5.5 mg, 0.005 mmol), 1,2-bis(dicyclohexylphosphino)ethane (6 mol%, 2.5 mg, 0.006 mmol) and 1 mL of dry diglyme. After stirring at room temperature for 5 minutes, acetophenone (12 mg, 0.1 mmol), phenylboroxine (16 mg, 0.05 mmol), water (0.2 μL , 10 mol%) and GC standard *n*-dodecane (10 μL) were then added sequentially. The tube was capped tightly and the reaction mixture was heated on an oil bath maintained at 110 $^\circ\text{C}$. At intervals, aliquots of the reaction mixture were taken in the glove box and passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of acetophenone and the yield of carbinol and final product.

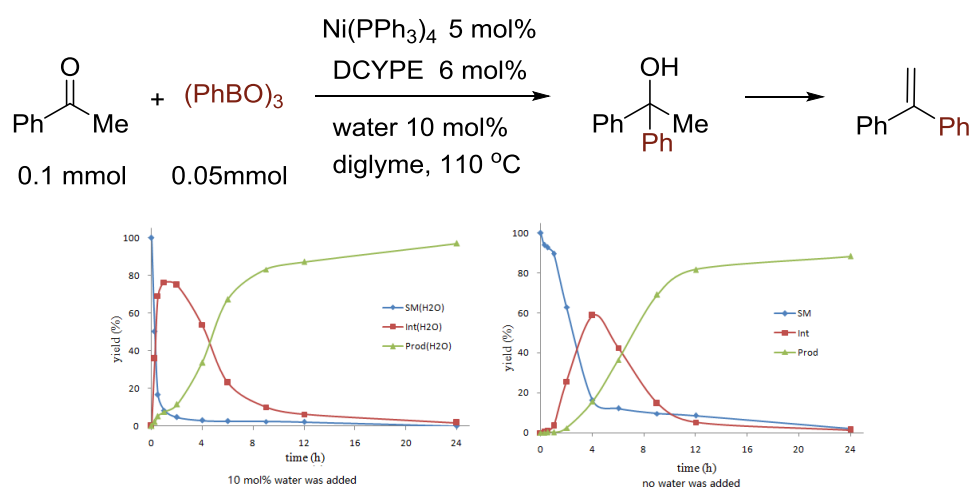


Figure S1. Reaction of acetophenone in the presence (left) and absence (right) of water

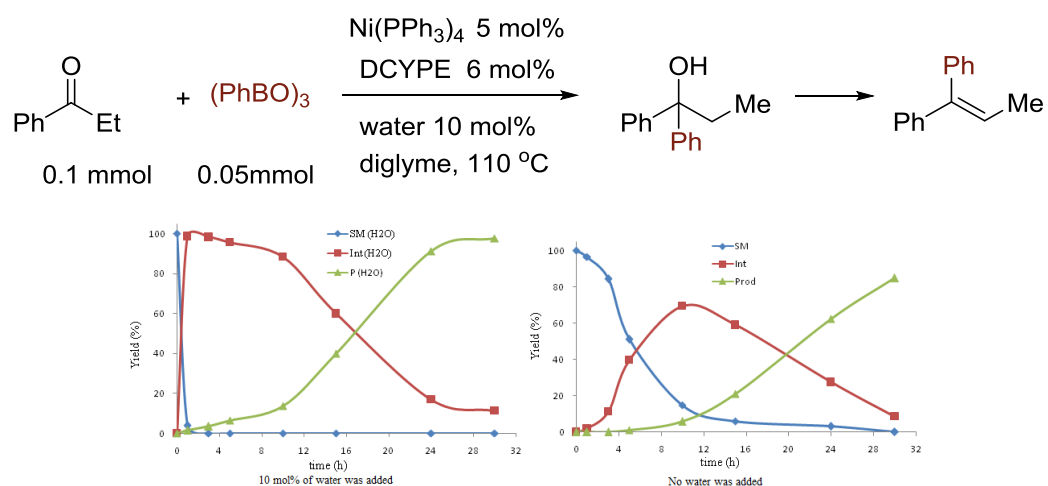


Figure S2. Reaction of propiophenone in the presence (left) and absence (right) of water

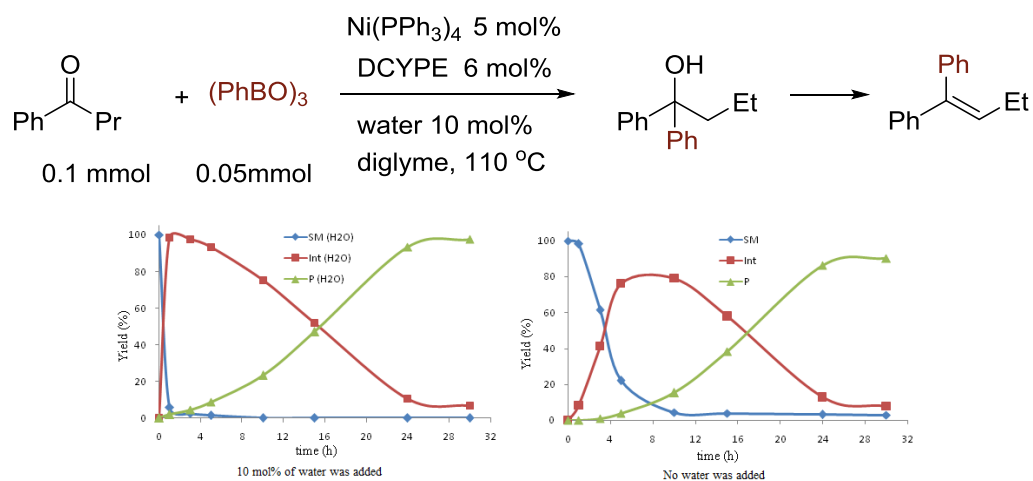
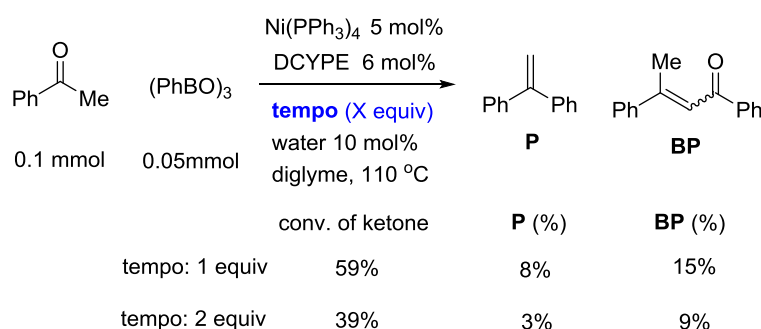


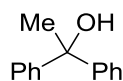
Figure S3. Reaction of butyrophenone in the presence (left) and absence (right) of water

(2) The model arylation reaction in the presence of TEMPO

It was conducted in the model catalytic reaction of acetophenone by adding TEMPO (16 mg, 0.1 mmol, 1 equiv). The tube was capped tightly and the reaction mixture was heated on an oil bath maintained at 110 °C for 1 day. At the end of the reaction, the mixture was cooled to room temperature. Aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of acetophenone and calibrated GC yield of product **P** and byproduct **BP**. No TEMPO-trapped compound was detected by GC and GCMS.



(3) Synthesis of d-labeled compounds



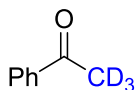
1-Methylbenzhydryl alcohol [599-67-7].³²

To a solution of acetophenone (1.2 g, 10 mmol) in 10 mL of THF was added PhMgBr (12 mmol, 1 M in THF) dropwise over 15 min at 0 °C. This reaction mixture was stirred at 0 °C for 2 h and then quenched by saturated aqueous NH₄Cl (10 mL). After routine workup, the product was purified by flash chromatography over silica gel using hexanes/EA (10:1) as the eluent to get the desired 1-methylbenzhydryl alcohol as a white solid (1.68 g, 85% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.41 (m, 4H), 7.35 – 7.30 (m, 4H), 7.27 – 7.23 (m, 2H), 2.21 (s, 1H), 1.97 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 148.2, 128.3, 127.1, 126.0, 76.4, 31.0.

MS (EI): Calcd for C₁₄H₁₄O: 198.1; found: 198.1.



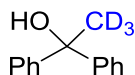
2,2,2-Trideuterioacetophenone (97% D).

2,2,2-Trideuterioacetophenone was synthesized according to a literature procedure.³³ A mixture of acetophenone (2.88 g, 24 mmol), NaOH (0.08 g, 2 mmol) and D₂O (99.9% D, CIL) (16.0 ml) was stirred at room temperature for 24 h under nitrogen. The reaction mixture was diluted with dry diethyl ether (10 mL). The aqueous layer was extracted with diethyl ether (10 mL x 3). The combined organic layer was dried over Na₂SO₄, filtered and concentrated. The crude product was deuterated one more time by repeating the procedure. The final residue was purified by flash chromatography over silica gel using hexanes as elute to afford the 2,2,2-trideuterioacetophenone as a colorless oil (2.5 g, 97% D, 85% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.58 – 2.57 (m, 0.09 H).

¹³C NMR (100 MHz, CDCl₃): δ 198.4, 137.3, 133.2, 128.7, 128.4.

MS (EI): Calcd for C₈H₅D₃O: 123.1; found: 123.0.



2,2,2-Trideuterio-1-methylbenzhydryl alcohol (97% D).

The 2,2,2-trideuterio-1-methylbenzhydryl alcohol was synthesized *via* addition of PhMgBr in THF to 2,2,2-trideuterioacetophenone (97% D) over 1h at 0 °C for 2 h. Isolated yield: 81%.

¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, *J* = 7.9 Hz, 4H), 7.31 (t, *J* = 7.6 Hz, 4H), 7.23 (t, *J* = 7.1 Hz, 2H), 2.19 (br s, 1H), 1.91 (m, 0.09 H).

¹³C NMR (100 MHz, CDCl₃): δ 148.1, 128.3, 127.1, 126.0, 76.2.

MS (EI): Calcd for C₁₄H₁₁D₃O: 201.1; found: 201.1.

(4) Elimination of the carbinol

A typical procedure for elimination: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with Ni(PPh₃)₄ (5 mol%, 5.5 mg, 0.005 mmol), 1,2-bis(dicyclohexylphosphino)ethane (6 mol%, 2.5 mg, 0.006 mmol) and 1 mL of dry diglyme. After stirring at room temperature for 5 minutes, 1-methylbenzhydryl alcohol (20 mg, 0.1 mmol), phenylboroxine (16 mg, 0.05 mmol), and GC standard *n*-dodecane (10 μL) were then added sequentially. The tube was capped tightly and the reaction mixture was heated in an oil bath maintained at 110 °C for a specific time, and aliquots of the reaction mixture were taken in a glove box and passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of the carbinol and the calibrated GC yield of olefin product.

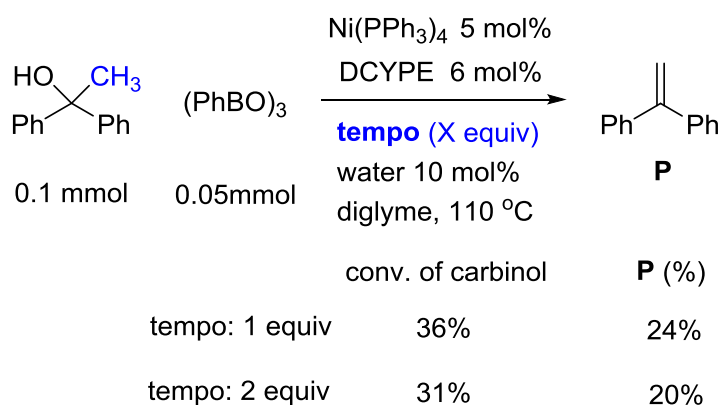
Table S8. Elimination of the carbinol

$ \begin{array}{c} \text{HO}-\text{C}(\text{CH}_3)(\text{Ph})_2 \\ \text{0.1 mmol} \end{array} \xrightarrow[\text{0.05mmol}]{\begin{array}{c} \text{(PhBO)}_3 \\ \text{Ni(PPh}_3)_4 \text{ 5 mol\%} \\ \text{DCYPE 6 mol\%} \\ \text{water 10 mol\%} \\ \text{diglyme, 110 }^\circ\text{C, 24 h} \end{array}} \begin{array}{c} \text{Ph}-\text{C}(\text{CH}_3)=\text{Ph} \\ \text{P} \end{array} $						
Entry	Ni(PPh ₃) ₄	DCYPE (mol%)	(PhBO) ₃ (equiv)	H ₂ O (%)	Conv of carbinol (%)	P (%)
1	0	0	0	0	4	0
2	5	6	0	0	1	0
3	0	6	0.5	0	7	2
4	5	0	0.5	0	14	7
5	5	6	0.5	0	99	97
6	5	6	0.3	0	82	81
7	5	6	0.16	0	20	14
8	0	6	0.5	10	9	3
9	5	0	0.5	10	12	6
10	5	6	0.5	10	99	88

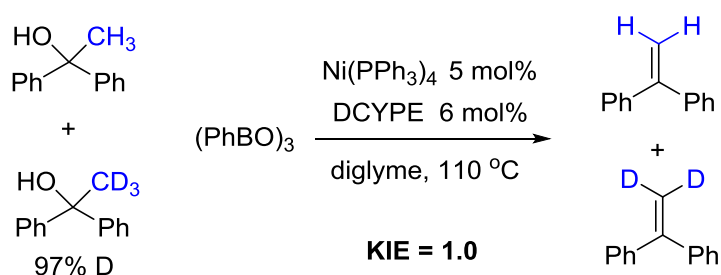
(5) Elimination of the carbinol in the presence of TEMPO

TEMPO (16 mg, 0.1 mmol) was added. The tube was capped tightly and the reaction mixture was heated on an oil bath maintained at 110 °C for 1 day. At the end of the reaction, the mixture was cooled to room temperature.

Aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of acetophenone and calibrated GC yield of product **P**.



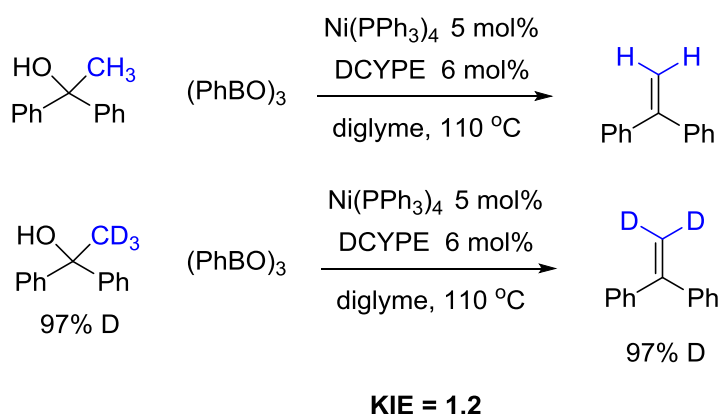
(6) Elimination of two carbinols: competition in one vessel



In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with Ni(PPh₃)₄ (5 mol%, 11 mg, 0.01 mmol), 1,2-bis(dicyclohexylphosphino)ethane (6 mol%, 5 mg, 0.012 mmol) and 2 mL of dry diglyme. After stirring at room temperature for 5 minutes, non-labeled carbinol (20 mg, 0.1 mmol) and d₃-carbinol (20 mg, 0.1 mmol), phenylboroxine (31 mg, 0.1 mmol), and GC standard *n*-dodecane (20 μL) were then added sequentially. The tube was capped tightly and the reaction mixture was heated on an oil bath maintained at 110 °C for 10 h (conversion of carbinols: 31% combined). The desired products were purified directly by flash chromatography over silica gel using hexanes as the eluent. The extent of deuteration was determined by quantitative ¹H NMR spectroscopy and the presence of deuterium in the products was confirmed by ²H NMR spectroscopy.

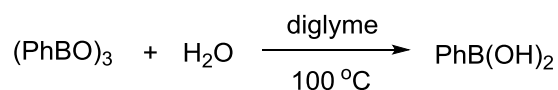
(7) Elimination of two carbinols in two separate vessels.

In an argon-filled glove box, a 10-mL Schlenk tube containing a magnet stir bar was charged with $\text{Ni}(\text{PPh}_3)_4$ (5 mol%, 5.5 mg, 0.005 mmol), 1,2-bis(dicyclohexylphosphino)ethane (6 mol%, 2.5 mg, 0.006 mmol) and 1 mL of dry diglyme. After stirring at room temperature for 5 minutes, carbinol (20 mg, 0.1 mmol), phenylboroxine (16 mg, 0.05 mmol), and GC standard *n*-dodecane (10 μL) were then added sequentially. In another tube, deuterated carbinol (20 mg, 0.1 mmol) was added instead. The two tubes were capped tightly and the reactions were heated on an oil bath maintained at 110 °C. At each time interval, aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrates were subjected to GC analysis for determination of the conversion of carbinols and the calibrated GC yields of olefinic products. The initial KIE value at 4 h was calculated to be 1.2



Products	4 h	8 h
non-labeled product (%)	4.4	25.0
d-labeled product (%)	3.7	24.8

(8) Hydrolysis of phenylboroxine in the presence of H₂O



A typical procedure: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with phenylboroxine (16 mg, 0.05 mmol), water (0.2 μL , 10 mol%) and 1 mL of nondeuteriated dry diglyme. The tube was capped tightly and the reaction mixture was heated in an oil bath maintained at 100 $^\circ\text{C}$ for 10 h. Then the reaction mixture was directly transferred to J Young NMR tube and analyzed by no-D proton NMR spectroscopy. ^{11}B NMR spectra gave broad peaks around 30 ppm for both phenylboroxine and phenylboronic acid, thus they gave no useful information of hydrolysis. A small amount of water was added to pure $\text{PhB}(\text{OH})_2$ to prevent partial dehydration to form $(\text{PhBO})_3$ in the dry diglyme.

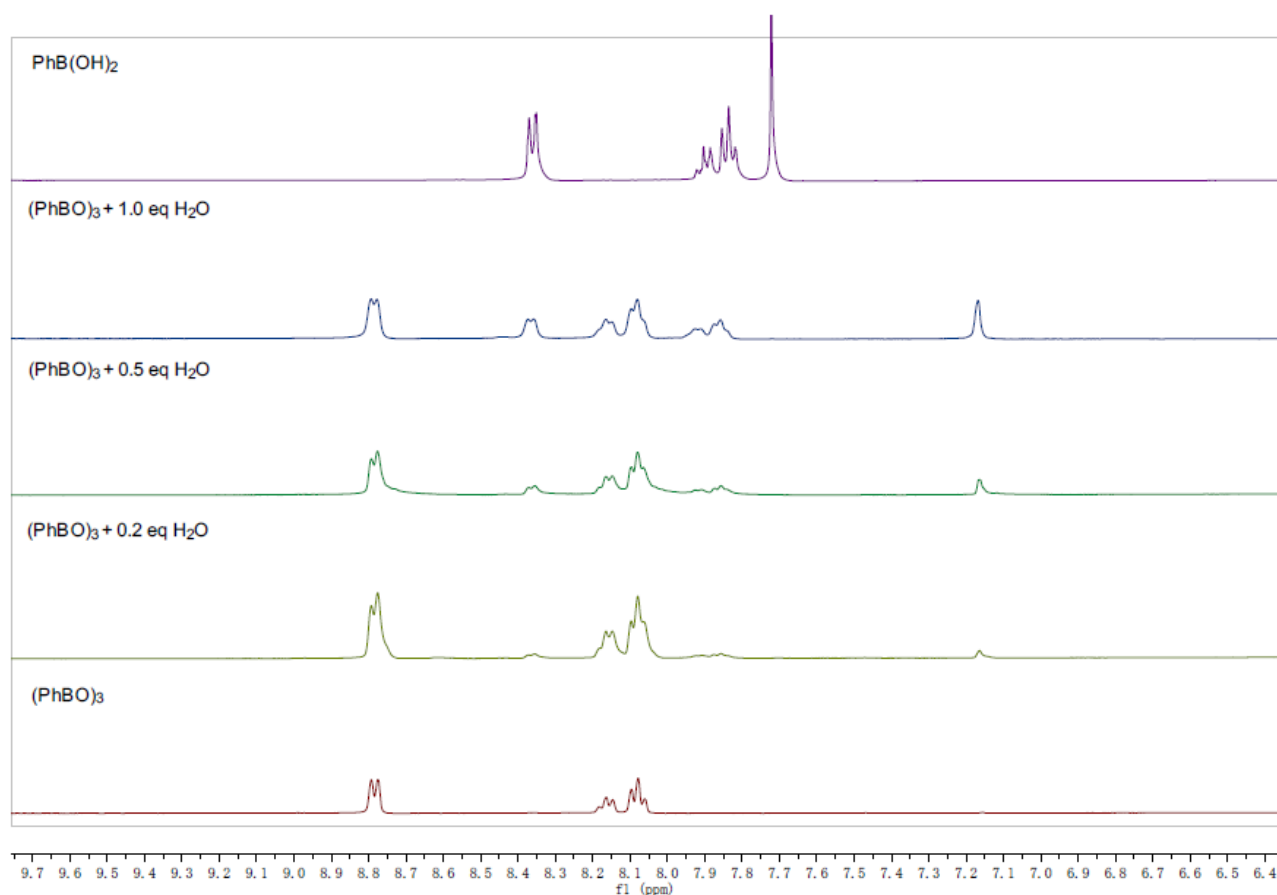
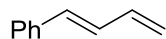


Figure S4 ^1H NMR spectra after hydrolysis with water

V. Compatibility and dehydration of added alcohols in model catalytic arylation

The model arylation reaction was conducted in the presence of an added alcohol (1 equiv). The Calibrated conversion and GC yields were calibrated with authentic samples.



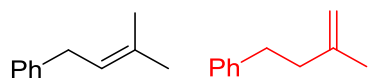
***trans*-1-Phenyl-1,3-butadiene (S1) [16939-57-4].³⁴**

Colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.43 – 7.41 (m, 2H), 7.35 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 6.81 (dd, *J* = 15.4, 10.7 Hz, 1H), 6.60 – 6.48 (m, 2H), 5.35 (d, *J* = 16.9 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 137.31, 137.26, 133.0, 129.8, 128.7, 127.8, 126.6, 117.8.

MS (EI): Calcd for C₁₀H₁₀: 130.1; found: 130.1.



3-Methyl-1-phenylbut-2-ene (S2) [4489-84-3]³⁵ and 2-methyl-4-phenyl-1-butene (S2') [6683-51-8].³⁶

Colorless oil.

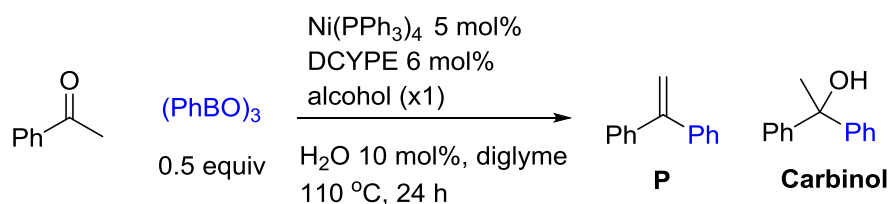
NMR for a mixture of two isomers:

¹H NMR (400 MHz, CDCl₃): δ 7.32 – 7.18 (m, 3H+4H), 5.38 – 5.34 (m, 1H), 4.77 (s, 0.4H), 4.74 (s, 0.4H), 3.37 (d, *J* = 7.3 Hz, 2H), 2.80 – 2.76 (m, 0.8H), 2.37 – 2.33 (m, 0.8H), 1.80 (s, 1.2H), 1.78 (s, 3H), 1.75 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 145.5, 142.4, 142.0, 132.6, 128.49, 128.45, 128.4, 125.9, 125.8, 123.4, 110.4, 39.8, 34.5, 34.4, 25.9, 22.7, 18.0.

MS (EI): Calcd for C₁₁H₁₄: 146.1; found: 146.1.

Table S9. Dehydration of alcohols in model catalytic arylation



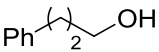
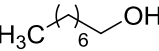
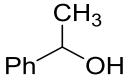
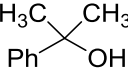
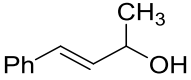
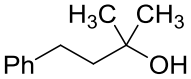
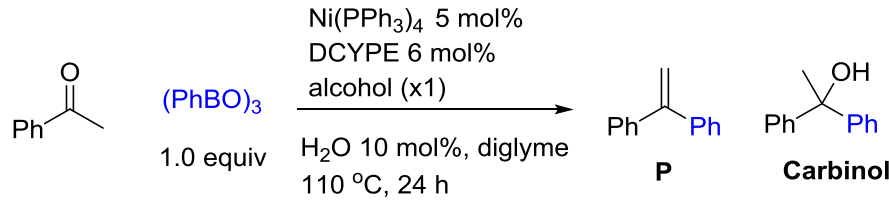
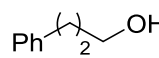
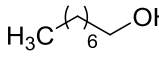
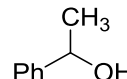
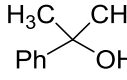
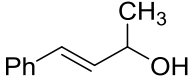
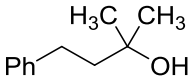
entry	Additive	Conv of ketone (%)	Carbinol (%)	P (%)	Conv of alcohol (%)	Dehydration of alcohol (%)
1		26	4	21	4	0
2		37	8	28	5	0
3		29	1	27	8	5
4		10	7	0	29	23
5		4	2	0	95	13
6		42	13	26	15	13 (isomers 1.5:1)

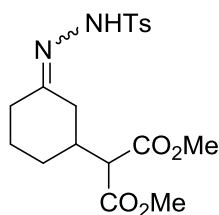
Table S10. Dehydration of alcohols in model catalytic arylation using 1 equiv of (PhBO)₃

<div style="display: flex; align-items: center; justify-content: space-around;"> <div style="text-align: center;">  </div> </div>						
entry	Additive	Conv. of ketone (%)	Carbinol (%)	P (%)	Conv. of Alcohol (%)	Dehydration of alcohol (%)
1		100	0	99	5	0
2		100	0	95	2	0
3		100	0	95	40	34
4		86	0	84	100	99
5		8	0	1	100	13
6		100	0	98	94	92 (isomers 1.1:1)

VI. Palladium-catalyzed arylation of hydrazones under Barluenga and related conditions

(a) Synthesis of tosylhydrazones

To a solution of *p*-toluenesulfonylhydrazide (2 mmol) in methanol (5 mL) was added ketone (2 mmol). The reaction mixture was stirred at rt for 24 h or refluxed overnight. After cooling, the tosylhydrazone was collected as crystal after filtration and washing with cold methanol.



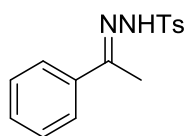
Dimethyl (3-oxocyclohexyl)malonate *p*-toluenesulfonylhydrazone (4a).

White solid. NMR for a mixture of both E and Z isomers:

^1H NMR (400 MHz, CDCl_3): δ 7.83 – 7.80 (m, 4H), 7.63 (br 2H), 7.31 – 7.29 (m, 4H), 3.74 – 3.71 (m, 12H), 3.22 (dd, J = 8.3, 1.9 Hz, 2H), 2.63 – 2.60 (m, 2H), 2.44 – 2.42 (m, 6H), 2.37 – 2.26 (m, 4H), 2.13 – 1.72 (m, 8H), 1.51 – 1.21 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.9, 168.6, 168.5, 160.2, 160.0, 144.1, 144.0, 135.5, 135.4, 129.7, 129.6, 128.2, 128.1, 56.7, 55.9, 53.0, 52.73, 52.68, 52.6, 38.6, 37.7, 37.0, 34.8, 30.3, 29.2, 26.2, 24.8, 23.9, 21.7.

MS (ESI): Calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_6\text{S}$ $[\text{M}+\text{H}]^+$: 397.1; found: 397.1.



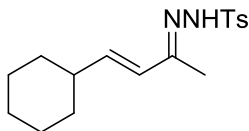
Acetophenone *p*-toluenesulfonylhydrazone (4b) [4545-21-5].³⁷

White solid.

^1H NMR (400 MHz, CDCl_3): δ 8.07 (br s, 1H), 7.93 (d, J = 7.9 Hz, 2H), 7.65 – 7.64 (m, 2H), 7.34 – 7.31 (m, 5H), 2.41 (s, 3 H), 2.16 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ 152.7, 144.3, 137.4, 135.6, 129.74, 129.71, 128.5, 128.3, 126.4, 21.7, 13.5.

MS (ESI): Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 289.1; found: 289.2.



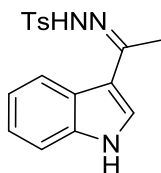
(*E*)-4-Cyclohexylbut-3-en-2-one *p*-toluenesulfonylhydrazone (4c).

White solid.

^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 8.3 Hz, 2H), 7.70 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 6.08 (dd, J = 16.2, 0.9 Hz, 1H), 5.96 (dd, J = 16.2, 6.6 Hz, 1H), 2.42 (s, 3H), 2.08 – 1.98 (m, 1H), 1.84 (s, 3H), 1.74 – 1.63 (m, 5H), 1.31 – 1.02 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3): δ 154.3, 144.1, 143.0, 135.6, 129.7, 128.2, 128.0, 41.0, 32.6, 26.1, 26.0, 21.7, 11.4.

MS (ESI): Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 321.2; found: 321.2.



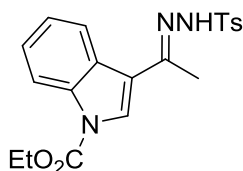
3-Acetylindole *p*-toluenesulfonylhydrazone (4d) [342388-23-2].

White solid.

^1H NMR (400 MHz, d_4 -MeOD): δ 8.08 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.3 Hz, 2H), 7.55 (s, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.04 – 7.00 (m, 1H), 2.38 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, d_4 -MeOD): δ 153.6, 143.7, 137.3, 136.4, 129.0, 128.0, 126.8, 124.7, 122.8, 122.0, 119.9, 114.8, 110.7, 20.1, 13.5.

MS (ESI): Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 328.1; found: 328.2.



***N*-Ethoxycarbonyl 3-acetylindole *p*-toluenesulfonylhydrazone (4e).**

White solid.

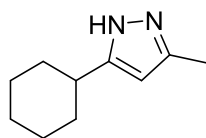
^1H NMR (300 MHz, CDCl_3): δ 8.28 (d, J = 7.5 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 8.00 – 7.96 (m, 3H), 7.76 (s, 1H), 7.39 – 7.26 (m, 4H), 4.50 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 2.18 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 150.8, 149.3, 144.4, 136.1, 135.6, 129.8, 128.3, 127.4, 126.5, 125.5, 123.9, 120.1, 114.9, 63.8, 21.7, 14.5, 14.2.

MS (ESI): Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 400.1; found: 400.2.

(b) Palladium-catalyzed arylation of hydrazones

A typical procedure based on Barluenga conditions: In an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with $\text{Pd}_2(\text{dba})_3$ (2 mol %, 1.8 mg, 0.002 mmol), dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (4 mol %, 1.9 mg, 0.004 mmol), LiO^tBu (19 mg, 0.24 mmol), tosylhydrazone (0.1 mmol), dry dioxane (1 mL) and GC standard *n*-dodecane (10 μL). After stirring for 5 minutes, aryl halide (0.1 mmol) was then added. The tube was capped tightly and the reaction mixture was heated in an oil bath maintained at 110 $^\circ\text{C}$ for 15 h. At the end of the reaction, the mixture was cooled to room temperature. Saturated NH_4Cl solution (1 mL) was added to neutralize the reaction, and then aliquots of the reaction mixture were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the conversion of aryl halide and calibrated yield of the product and byproducts. Hydrazones cannot be detected by GC, so TLC was used to check whether some hydrazine remained in the reaction mixtures.



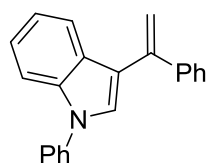
3-Methyl-5-cyclohexylpyroazole (5b) [152307-48-7].³⁸

Colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 10.37 (br s, 1H), 5.82 (s, 1H), 2.65 – 2.59 (m, 1H), 2.27 (s, 3H), 1.98 – 1.96 (m, 2H), 1.81 – 1.78 (m, 2H), 1.72 – 1.69 (m, 1H), 1.44 – 1.21 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3): δ 153.9, 144.6, 101.2, 36.4, 33.2, 26.4, 26.1, 12.6.

MS (EI): Calcd for $\text{C}_{10}\text{H}_{16}\text{N}_2$: 164.1; found: 164.1.



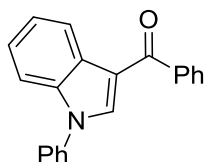
N-Phenyl 3-(1-styryl)indole (5c).

Colorless oil. The compound was quickly oxidized by air to form a ketone in CDCl_3 (untreated with base).

^1H NMR (400 MHz, d_4 -MeOD): δ 7.56 – 7.51 (m, 5H), 7.47 – 7.45 (m, 2H), 7.39 – 7.31 (m, 6H), 7.20 – 7.16 (m, 1H), 7.06 – 7.02 (m, 1H), 5.59 (d, J = 1.6 Hz, 1H), 5.43 (d, J = 1.7 Hz, 1H).

^{13}C NMR (100 MHz, d_4 -MeOD): δ 143.3, 142.2, 139.4, 136.6, 129.4, 127.8, 127.6, 127.4, 127.3, 126.4, 124.0, 122.3, 120.5, 120.1, 118.7, 111.4, 110.2.

MS (EI): Calcd for $\text{C}_{22}\text{H}_{17}\text{N}$: 295.1; found: 295.2.



***N*-Phenyl 3-benzoylindole (5d) [113963-64-7].³⁹**

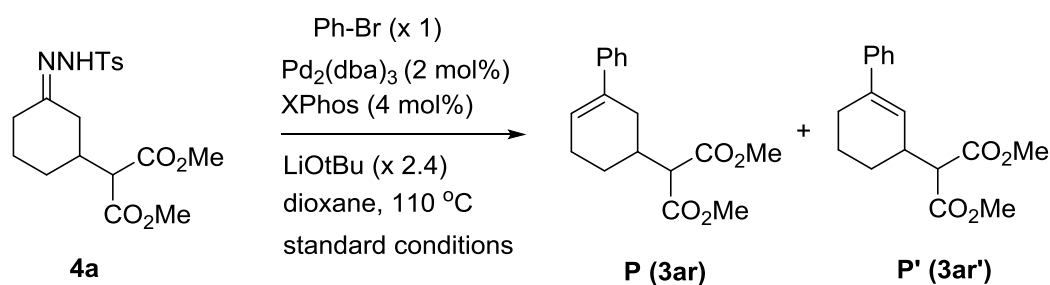
Pale yellow solid.

^1H NMR (CDCl_3 , 400 MHz): δ 8.52 – 8.50 (m, 1 H), 7.90 – 7.87 (m, 2 H), 7.78 (s, 1 H), 7.58 – 7.48 (m, 9 H), 7.47 – 7.35 (m, 2 H);

^{13}C NMR (CDCl_3 , 100 MHz): δ 191.3, 140.8, 138.5, 137.3, 136.8, 131.5, 130.0, 128.9, 128.5, 128.2, 127.7, 125.1, 124.4, 123.4, 123.1, 117.5, 111.0.

MS (EI): Calcd for $\text{C}_{21}\text{H}_{15}\text{NO}$: 297.1; found: 297.1.

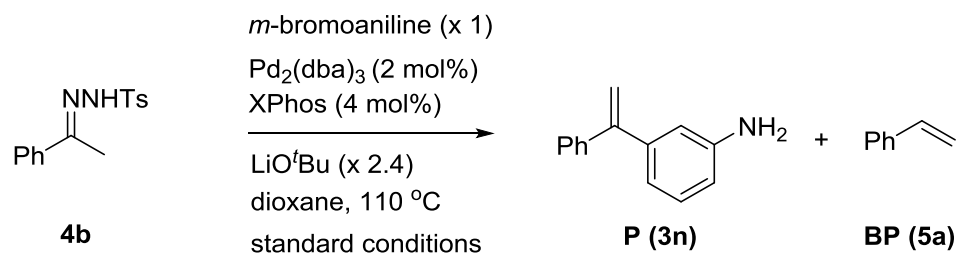
Table S11. Arylation of a hydrazone carrying a malonate group



Entry	Pd source	Phosphine	Base	Solvent	Temp. (°C)	Conv. of ArBr (%)	Conv. of hydrazone (%)	P+P' (%)	P:P'
1 ^[a]	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	Dioxane	110	85	100	54	1.2:1
2	Pd ₂ (dba) ₃	XPhos	NaO ^t Bu	Dioxane	110	78	100	28	1.4:1
3	Pd ₂ (dba) ₃	XPhos	KO ^t Bu	Dioxane	110	82	100	14	1:1.1
4	Pd ₂ (dba) ₃	XPhos	CS ₂ CO ₃	Dioxane	110	37	100	14	2:1
5	Pd ₂ (dba) ₃	XPhos	Na ₂ CO ₃	Dioxane	110	25	100	0	0
6	Pd ₂ (dba) ₃	XPhos	K ₃ PO ₄	Dioxane	110	24	100	12	1.9:1
7 ^[b]	Pd(OAc) ₂	XPhos	LiO ^t Bu	Dioxane	110	100	100	50	1.3:1
8	PdCl ₂	XPhos	LiO ^t Bu	Dioxane	110	98	100	51	1.3:1
9	PdCl ₂ (CH ₃ CN) ₂	XPhos	LiO ^t Bu	Dioxane	110	98	100	49	1.3:1
10	Pd ₂ (dba) ₃	JohnPhos	LiO ^t Bu	Dioxane	110	95	100	50	1:1
11	Pd ₂ (dba) ₃	SPhos	LiO ^t Bu	Dioxane	110	96	100	56	1.2:1
12	Pd ₂ (dba) ₃	PtBu ₃	LiO ^t Bu	Dioxane	110	100	100	38	1.4:1
13	Pd ₂ (dba) ₃	PCy ₃	LiO ^t Bu	Dioxane	110	94	100	68	1:1.1
14	Pd ₂ (dba) ₃	DPPF	LiO ^t Bu	Dioxane	110	49	100	32	1:1.3
15	Pd ₂ (dba) ₃	DPPP	LiO ^t Bu	Dioxane	110	49	100	31	1:2.2
16	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO ^t Bu	Dioxane	110	69	100	30	1:1
17 ^[c]	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO ^t Bu	Toluene	110	9	100	5	2.3:1
18	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	THF	110	18	100	4	1:1.8
19	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	DME	110	60	100	27	1:1
20	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu (x4)	Dioxane	110	100	100	50	1:1

[a] Barluenga's condition: equimolar of ArX and hydrazone, Pd₂(dba)₃ (1 mol%), XPhos (2 mol%), LiO^tBu (2.2 equiv) in dioxane at 70-110 °C, see ref 40. [b] Alami's condition: equimolar of ArX and hydrazone, Pd(OAc)₂ (5 mol%), XPhos (10 mol%), LiO^tBu (2.0 equiv) in dioxane at 90 °C, see ref 41. [c] Wang's condition, equimolar of ArX and hydrazone, Pd₂(dba)₃ (2.5 mol%), P(2-furyl)₃ (20 mol%), LiO^tBu (3 equiv) in toluene at 80 °C, see ref 42.

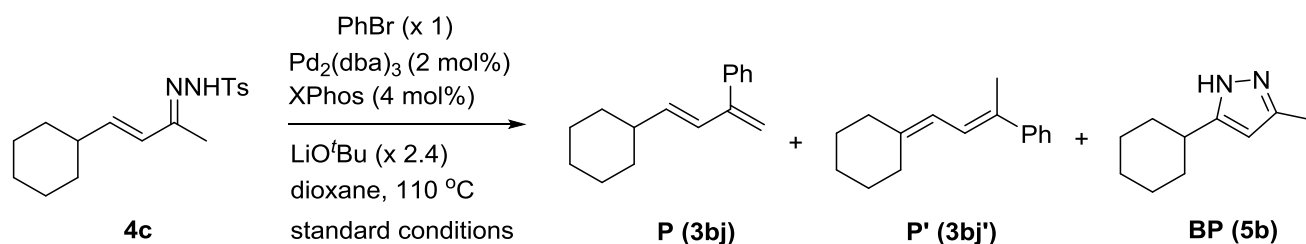
Table S12. Arylation of a hydrazone with 3-bromoaniline



Entry	Pd source	Phosphine	Base	Solvent	Temp (°C)	Conv of ArBr (%)	Conv of hydrazone (%)	P (%)	BP (%)
1 ^[a]	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	Dioxane	110	100	100	6	29
2	Pd ₂ (dba) ₃	XPhos	NaO ^t Bu	Dioxane	110	100	100	0	62
3	Pd ₂ (dba) ₃	XPhos	KO ^t Bu	Dioxane	110	100	100	0	13
4	Pd ₂ (dba) ₃	XPhos	CS ₂ CO ₃	Dioxane	110	64	100	8	9
5	Pd ₂ (dba) ₃	XPhos	Na ₂ CO ₃	Dioxane	110	42	100	12	1
6	Pd ₂ (dba) ₃	XPhos	K ₃ PO ₄	Dioxane	110	58	100	41	1
7	Pd(OAc) ₂	XPhos	LiO ^t Bu	Dioxane	110	100	majority	28	31
8	PdCl ₂	XPhos	LiO ^t Bu	Dioxane	110	100	100	9	39
9	PdCl ₂ (CH ₃ CN) ₂	XPhos	LiO ^t Bu	Dioxane	110	100	majority	23	34
10	Pd ₂ (dba) ₃	Johnphos	LiO ^t Bu	Dioxane	110	100	100	3	8
11	Pd ₂ (dba) ₃	SPhos	LiO ^t Bu	Dioxane	110	100	100	25	29
12	Pd ₂ (dba) ₃	tBu-XPhos	LiO ^t Bu	Dioxane	110	100	100	2	10
13	Pd ₂ (dba) ₃	PtBu ₃	LiO ^t Bu	Dioxane	110	100	100	7	0
14	Pd ₂ (dba) ₃	DPPF	LiO ^t Bu	Dioxane	110	100	100	37	1
15	Pd ₂ (dba) ₃	DPPP	LiO ^t Bu	Dioxane	110	66	majority	18	7
16	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO ^t Bu	Dioxane	110	68	100	14	0
17	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO ^t Bu	Toluene	110	56	100	25	29
18	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	THF	110	100	100	5	54
19	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	DME	110	100	100	23	29
20	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu (x4)	Dioxane	110	100	100	0	42
21 ^[b]	PdCl ₂ (PPh ₃) ₂	None	LiO ^t Bu (x4)	Dioxane	100	95	100	51	5

[a] Barluenga's condition: equimolar of ArX and hydrazone, Pd₂(dba)₃ (1 mol%), XPhos (2 mol%), LiO^tBu (2.2 equiv) in dioxane at 70-110 °C, see ref 40. [b] Prabhu's condition: equimolar of ArX and hydrazone, PdCl₂(PPh₃)₂ (2.5 mol%), LiO^tBu (4 equiv) in dioxane at 100 °C, see ref 43.

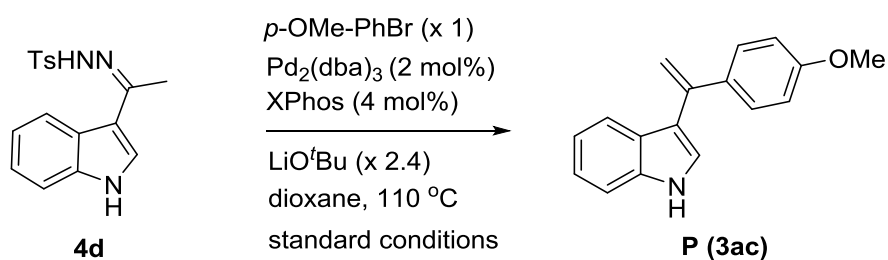
Table S13. Arylation of α,β -unsaturated hydrazone. The reactions gave a pyrazole as main byproduct



Entry	Pd source	Phosphine	Base	Solvent	Temp (°C)	Conv of ArBr (%)	Conv of hydrazone (%)	P+P' (%)	BP (%)
1 ^[a]	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	Dioxane	110	7	100	3 (1:1.7)	85
2	Pd ₂ (dba) ₃	XPhos	NaO ^t Bu	Dioxane	110	1	100	0	97
3	Pd ₂ (dba) ₃	XPhos	KO ^t Bu	Dioxane	110	11	100	0	86
4	Pd ₂ (dba) ₃	XPhos	Cs ₂ CO ₃	Dioxane	110	4	100	0	98
5	Pd ₂ (dba) ₃	XPhos	Na ₂ CO ₃	Dioxane	110	9	100	0	53
6	Pd ₂ (dba) ₃	XPhos	K ₃ PO ₄	Dioxane	110	0	100	0	86
7	Pd(OAc) ₂	XPhos	LiO ^t Bu	Dioxane	110	0	100	0	83
8	PdCl ₂	XPhos	LiO ^t Bu	Dioxane	110	0	100	0	78
9	PdCl ₂ (CH ₃ CN) ₂	XPhos	LiO ^t Bu	Dioxane	110	0	100	0	79
10	Pd ₂ (dba) ₃	JohnPhos	LiO ^t Bu	Dioxane	110	21	100	5 (1:1.8)	79
11	Pd ₂ (dba) ₃	SPhos	LiO ^t Bu	Dioxane	110	0	100	0	89
12	Pd ₂ (dba) ₃	PtBu ₃	LiO ^t Bu	Dioxane	110	1	100	0	87
13	Pd ₂ (dba) ₃	PCy ₃	LiO ^t Bu	Dioxane	110	3	100	2 (1:1.7)	86
14	Pd ₂ (dba) ₃	DPPF	LiO ^t Bu	Dioxane	110	0	100	0	92
15	Pd ₂ (dba) ₃	DPPP	LiO ^t Bu	Dioxane	110	0	100	0	99
16	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO ^t Bu	Dioxane	110	0	100	0	82
17	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO ^t Bu	Toluene	110	0	100	0	69
18	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	THF	110	10	100	7 (1:3.4)	62
19	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu	DME	110	0	100	0	82
20	Pd ₂ (dba) ₃	XPhos	LiO ^t Bu (x4)	Dioxane	110	9	100	5 (1:1.2)	88

[a] Barluenga's condition: equimolar of ArX and hydrazone, Pd₂(dba)₃ (1 mol%), XPhos (2 mol%), LiO^tBu (2.2 equiv), in dioxane at 70-110 °C, see ref 40.

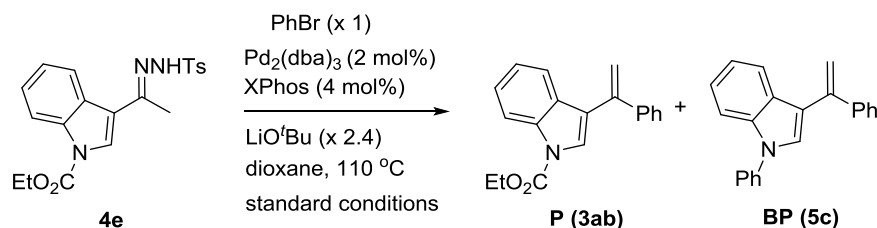
Table S14. Arylation of a hydrazone carrying an NH-indole ring. The reactions resulted in very complex mixtures, which accounted for material balance.



Entry	Pd source	Phosphine	Base	Solvent	Temp (°C)	Conv of ArBr (%)	Conv of hydrazone (%)	P (%)
1 ^[a]	$\text{Pd}_2(\text{dba})_3$	XPhos	LiO^tBu	Dioxane	110	100	100	0
2	$\text{Pd}_2(\text{dba})_3$	XPhos	NaO^tBu	Dioxane	110	43	partial	0
3	$\text{Pd}_2(\text{dba})_3$	XPhos	KO^tBu	Dioxane	110	2	majority	0
4	$\text{Pd}_2(\text{dba})_3$	XPhos	Cs_2CO_3	Dioxane	110	14	100	0
5	$\text{Pd}_2(\text{dba})_3$	XPhos	Na_2CO_3	Dioxane	110	7	majority	0
6	$\text{Pd}_2(\text{dba})_3$	XPhos	K_3PO_4	Dioxane	110	26	majority	0
7	$\text{Pd}(\text{OAc})_2$	XPhos	LiO^tBu	Dioxane	110	100	100	3
8	PdCl_2	XPhos	LiO^tBu	Dioxane	110	89	100	0
9	$\text{PdCl}_2(\text{CH}_3\text{CN})_2$	XPhos	LiO^tBu	Dioxane	110	95	100	0
10	$\text{Pd}_2(\text{dba})_3$	Johnphos	LiO^tBu	Dioxane	110	100	100	3
11	$\text{Pd}_2(\text{dba})_3$	SPhos	LiO^tBu	Dioxane	110	71	100	0
12	$\text{Pd}_2(\text{dba})_3$	PtBu_3	LiO^tBu	Dioxane	110	100	majority	6
13	$\text{Pd}_2(\text{dba})_3$	PCy_3	LiO^tBu	Dioxane	110	11	100	6
14	$\text{Pd}_2(\text{dba})_3$	DPPF	LiO^tBu	Dioxane	110	0	100	0
15	$\text{Pd}_2(\text{dba})_3$	DPPP	LiO^tBu	Dioxane	110	2	100	0
16	$\text{Pd}_2(\text{dba})_3$	$\text{P}(2\text{-furyl})_3$	LiO^tBu	Dioxane	110	32	100	5
17	$\text{Pd}_2(\text{dba})_3$	$\text{P}(2\text{-furyl})_3$	LiO^tBu	Toluene	110	14	100	0
18	$\text{Pd}_2(\text{dba})_3$	XPhos	LiO^tBu	THF	110	71	100	0
19	$\text{Pd}_2(\text{dba})_3$	XPhos	LiO^tBu	DME	110	79	100	0
20	$\text{Pd}_2(\text{dba})_3$	XPhos	$\text{LiO}^t\text{Bu}(\times 4)$	Dioxane	110	100	100	3

[a] Barluenga's condition: equimolar of ArX and hydrazone, $\text{Pd}_2(\text{dba})_3$ (1 mol%), XPhos (2 mol%), LiO^tBu (2.2 equiv), in dioxane at 70-110 °C, see ref 40.

Table S15. Arylation of a hydrazone carrying an *N*-carbamoyl indole. The reactions resulted in very complex mixtures, which accounted for material balance.



Entry	Pd source	Phosphine	Base	Solvent	Temp (°C)	Conv of ArBr (%)	Conv of hydrazone (%)	P (%)	BP (%)
1 ^[a]	Pd ₂ (dba) ₃	XPhos	LiO'Bu	Dioxane	90	37	100	0	4
2	Pd ₂ (dba) ₃	XPhos	LiO'Bu	Dioxane	110	100	100	0	24
3	Pd ₂ (dba) ₃	XPhos	NaO'Bu	Dioxane	110	99	100	0	14
4	Pd ₂ (dba) ₃	XPhos	KO'Bu	Dioxane	110	31	100	0	0
5	Pd ₂ (dba) ₃	XPhos	Cs ₂ CO ₃	Dioxane	110	18	100	2	0
6	Pd ₂ (dba) ₃	XPhos	Na ₂ CO ₃	Dioxane	110	17	100	4	0
7	Pd ₂ (dba) ₃	XPhos	K ₃ PO ₄	Dioxane	110	25	Partial	4	0
8	Pd(OAc) ₂	XPhos	LiO'Bu	Dioxane	90	57	100	0	12
9	Pd(OAc) ₂	XPhos	LiO'Bu	Dioxane	110	100	100	0	21
10	PdCl ₂	XPhos	LiO'Bu	Dioxane	110	100	100	0	12
11	Pd(PPh ₃) ₄	None	LiO'Bu	Dioxane	110	100	100	0	0
12	Pd ₂ (dba) ₃	Johnphos	LiO'Bu	Dioxane	110	100	100	1	34
13	Pd ₂ (dba) ₃	SPhos	LiO'Bu	Dioxane	110	100	100	0	16
14	Pd ₂ (dba) ₃	PtBu ₃	LiO'Bu	Dioxane	110	91	100	9	7
15	Pd ₂ (dba) ₃	PCy ₃	LiO'Bu	Dioxane	110	93	100	2	0
16	Pd ₂ (dba) ₃	DPPF	LiO'Bu	Dioxane	110	68	100	0	0
17	Pd ₂ (dba) ₃	DPPP	LiO'Bu	Dioxane	110	34	100	0	0
18	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO'Bu	Dioxane	110	79	100	0	0
19	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO'Bu	Toluene	80	25	100	3	0
20	Pd ₂ (dba) ₃	P(2-furyl) ₃	LiO'Bu	Toluene	110	38	100	1	0
21	Pd ₂ (dba) ₃	XPhos	LiO'Bu	THF	110	95	100	0	19
22	Pd ₂ (dba) ₃	XPhos	LiO'Bu	DME	110	78	100	0	18
23	Pd ₂ (dba) ₃	XPhos	LiO'Bu (x4)	Dioxane	110	100	100	0	27
24	Pd ₂ (dba) ₃	XPhos	Cs ₂ CO ₃ (x4)	Dioxane	110	29	100	4	0
25	Pd ₂ (dba) ₃	XPhos	K ₃ PO ₄ (x4)	Dioxane	110	17	100	4	0

[a] Barluenga's condition: equimolar of ArX and hydrazone, Pd₂(dba)₃ (1 mol%), XPhos (2 mol%), LiO'Bu (2.2 equiv), in dioxane at 70-110 °C, see ref 40

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